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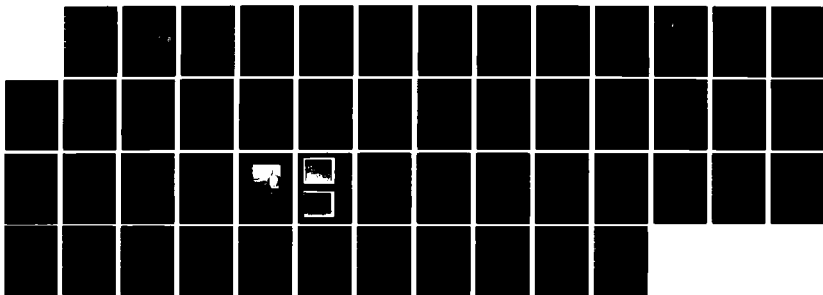
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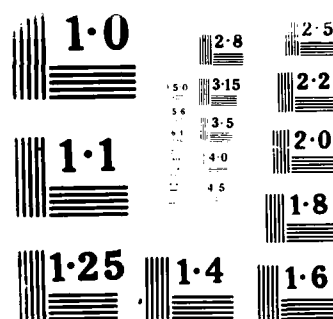
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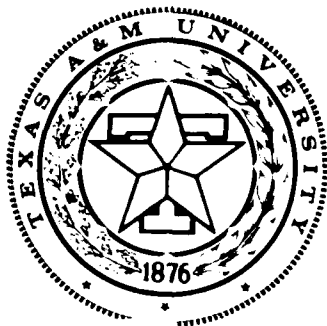
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COUPLED DAMAGE AND MOISTURE-TRANSPORT IN  
FIBER-REINFORCED POLYMERIC COMPOSITES

BY  
Y. WEITSMAN

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COUPLED DAMAGE AND MOISTURE-TRANSPORT  
IN FIBER-REINFORCED, POLYMERIC COMPOSITES.

By  
Y. Weitsman\*

Abstract

This paper presents a mathematical model for the coupling between moisture diffusion and damage in fiber-reinforced, polymeric composites. In these materials, moisture was observed to cause damage by a multitude of minute debondings at the fiber/matrix interfaces. The model employs concepts of continuum damage theory to describe those debondings. Formal evolutionary expressions are derived and related to the extent of damage, the stress field, moisture content and moisture gradient. The effects of damage on moisture diffusion and on reductions in moduli are also formulated.

Qualitative comparisons with experimental results are provided.

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## Introduction

It is well known that in many materials deformation under loads is associated with the formation of a multitude of internal flaws. These flaws, which may be micro voids, micro cracks or micro crazes, precede the development of macro cracks which cause final failure. The abovementioned flaws can be caused by environmental agents such as moisture and temperature, in addition to mechanical loads.

In the many circumstances where the micro flaws are distributed in a statistically homogeneous manner it is advantageous to represent them as internal state variables and employ thermodynamic considerations to establish constitutive relations and evolutionary expressions for flaw growth<sup>[1]\*,[2]</sup>. This approach is employed by several "continuum damage" models which were reviewed recently by D. Krajcinovic<sup>[3]</sup>. Guided by various physical and mathematical considerations, the internal state variables were chosen to be scalars, vectors, and tensors of various ranks. The case of a vector valued internal state variable was employed by Talreja<sup>[4],[5]</sup> to model damage in fiber reinforced composite laminates and relate stiffness reductions to external loads. More recently, a revision in the interpretation of "damage" as micro-crack areas lead to the selection of internal state variables as axial vectors (or, equivalently, as skew symmetric tensors).<sup>[6]</sup> This choice will also be employed in the present work.

Since the present investigation aims specifically at fibrous composites, where damage forms in characteristic patterns, the existence of

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\*Numbers in brackets indicate reference listed at the end of this paper.

a "representative damaged cell" is assumed. The components of the axial vector which represents "damage" are then defined as the projections of the total area of microcracks contained within the cell on its "walls". When those projections are divided by the respective areas of the cell's walls the measure of damage is non-dimensional. The representation of all the microcracks within a cell by a single axial vector certainly obscures the distinction between few "large" microcracks and many smaller microcracks. However, in circumstances when damage forms in consistent patterns such a distinction may not be important because the variability in microcrack sizes is likely to be limited. The interactions between microcracks within the cell will certainly depend on the external loads. It will be shown that the present model accounts for this dependence through stress-related damage-evolution relations.

With few exceptions<sup>[7]</sup>, most existing continuum damage formulations employ linearization in the damage parameters. By contrast, the present formulation does not involve series expansions in the damage parameter and is not limited to "small" damage.

In the presence of sharp gradients of temperature or moisture content, the expansional strains may be highly non-uniform within the characteristic damaged cell. In this case the stresses are likely to vary even along each of the individual microcracks, resulting in elevated stress-intensity factors at the microcrack tips. Within the context of a continuum damage theory these increases in stress-intensity are reflected in gradient-dependent damage evolution relations. Such relations are also considered in the present paper.

The effects of moisture in polymeric composites were investigated over more than a decade. A comprehensive review which appeared recently<sup>[8]</sup>

listed more than three hundred references on the subject. Damage due to moisture, which developed as debondings at the fiber/matrix interfaces, was observed by several investigators<sup>[9]-[17]</sup>. This typical form of moisture-induced damage was attributed to the presence of hygrophilic chemical agents at the fibers' surfaces<sup>[9]</sup>. Since the epoxy may act as a semi-permeable membrane, the high concentrations of moisture result in excessive osmotic pressures at the interfaces, leading to fiber/matrix debondings.

In another study<sup>[18]</sup> it was shown that epoxy resins absorbed excessive contents of moisture when the amount of curing agent in the mixture was below stoichiometry. Since it is plausible to assume that the stoichiometry of the resin would change in the vicinity of the fiber interfaces it is conceivable that the interphase regions contain excessive levels of moisture, which cause interfacial cracking.

The process of moisture sorption is associated with a thermodynamically "open" system, since vapor mass is being added to the material volume of the composite. This process will be accommodated in the present paper by considering a hypothetical vapor reservoir which is in thermodynamic equilibrium with the actual vapor contained in a material volume-element of the composite.

This approach follows the ideas employed by Biot<sup>[19]-[21]</sup> in connection with flow through porous media. It should be pointed out that in spite of the similarity between Biot's approach and the present formulation the two are not identical. The natural internal variable in Biot's scheme is the pore pressure, while in the present work it is more suitable to employ moisture content, or alternately the chemical potential. The subtle differences between the two formulations were pointed out by Gurtin<sup>[22]</sup>.



## 2. Basic Equations

Consider a solid body B occupying a material volume V bounded by a surface A. Let the solid, of mass density  $\rho_s$ , absorb vapor through its boundary and let  $\dot{m}$  denote the vapor-mass per unit volume of the solid. Also, let  $\underline{x}$  be the position of a solid mass particle in the deformed configuration that corresponds to the place  $\underline{X}$  in the undeformed state, and let  $\underline{f}$ ,  $\underline{q}$  and  $\underline{v}$  denote fluxes of vapor-mass and of heat, and the velocity of the solid particles, respectively.

In addition, let  $u$  and  $s$  be the internal energy and entropy densities of the solid/vapor mixture per unit solid mass, and let  $\sigma_{ij}$  and  $T$  denote the components of the Cauchy stress due to mechanically applied loads, and temperature, respectively.

A proper accounting of the state of the solid/vapor mixture, which is a thermodynamically open system, is obtained by considering each element in thermodynamic equilibrium with a reservoir containing vapor at pressure  $\hat{p}$ , density  $\hat{\rho}$ , and internal energy and entropy densities  $\hat{u}$  and  $\hat{s}$  respectively [20], [23], [24].

Conservation of the solid and vapor masses gives

$$\dot{\rho}_s + \rho_s \nabla \cdot \underline{v} = 0 \quad (1)$$

$$\dot{\dot{m}} = -\nabla \cdot \underline{f} \quad (2)$$

Conservation of energy over B reads

$$\begin{aligned} \frac{d}{dt} \int_V \rho_s u \, dV &= \int_A \sigma_{ij} n_j v_i \, dA - \int_A q_i n_i \, dA \\ &\quad - \int_A \hat{p} \frac{f_i}{\hat{\rho}} n_i \, dA - \int_A \hat{u} f_i n_i \, dA \end{aligned} \quad (3)$$

The third integral on the right side of (3) expresses the mechanical power due to vapor flux, observing that  $f_i/\hat{s}$  corresponds to vapor velocity. The last integral in (3) expresses the rate of vapor-borne energy.

The entropy inequality reads

$$\frac{d}{dt} \int_V \rho_s s dV \geq \int_A -(q_i/T) n_i dA - \int_A \hat{s} f_i n_i dA \quad (4)$$

where the last integral in (4) expresses the rate of vapor-borne entropy.

Application of Green's theorem to (3) and (4), and employment of (2), yields

$$\rho_s \dot{u} = \sigma_{ij} v_{i,j} - q_{i,i} - \hat{h}_{,i} f_i + \hat{h} \dot{m} \quad (5)$$

and

$$\rho_s T \dot{s} \geq -q_{i,i} + (q_i/T) g_i - T \hat{s}_{,i} f_i + T \hat{s} \dot{m} \quad (6)$$

where  $\hat{h} = (\hat{p}/\hat{\rho}) + \hat{u}$  is the enthalpy of the vapor in the hypothetical reservoir and  $g_i = T_{,i}$

Elimination of  $q_{i,i}$  between (5) and (6) yields the following expression for the "reduced entropy inequality"

$$-\rho_s \dot{\psi} - \rho_s s \dot{T} + \sigma_{ij} v_{i,j} - (q_i/T) g_i + \hat{\mu} \dot{m} - f_i \hat{\mu}_{,i} - \hat{s} g_i f_i \geq 0 \quad (7)$$

In (7)  $\psi = u - Ts$  is the Helmholtz free energy and  $\hat{\mu} = \hat{h} - T\hat{s}$  is the chemical potential of the vapor in the hypothetical reservoir.

### 3. Distributed Damage

When materials possess a statistically homogeneous microstructure, their mechanical response is associated with the creation and growth of a multitude of internal flaws. For several types of material microstructure these micro flaws develop in characteristic patterns, until they finally coalesce to form a localized, dominant crack whose growth leads to ultimate failure. Some characteristic damage patterns are shown in Figs. 1 and 2 for a fibrous composite laminates of different lay-ups. [25], [26]. Patterned damage was also observed in concrete and in ceramic materials.

In the abovementioned circumstances it is possible to relate the distributed flaws to a characteristic material "cell" and express the damage by means of a continuous, internal state variable [27]. Such cells are overlaid on the damage patterns in Figs. 1 and 2.

For damage due to micro-cracking, the internal state variable can be selected to represent the projections of all micro-crack surfaces on the "walls" of the characteristic cell. Since areas are expressed as vector products of directed line-segments, the present choice leads to a mathematical representation of "damage" as a skew-symmetric, second rank tensor  $d_{[ij]}$ . The quantity  $d_{[ij]}$  may be viewed as non-dimensional, since it can be formed by dividing all projected micro-crack areas through the respective areas of the cell walls.

In the presence of hygrothermal effects, diffusion and damage phenomena are likely to depend on gradients of moisture content  $\partial m / \partial x_i$  and of the temperature  $\partial T / \partial x_i$ . Upon consideration of the abovementioned characteristic cell it is possible to relate the latter dependencies to non-dimensional gradients  $\partial m / \partial \xi_i$  and  $\partial T / \partial \xi_i$ , where  $\xi_i = x_i / L_i$  (no sum on  $i$ ), with  $L_i$  being the lengths of the cell sides. [27]

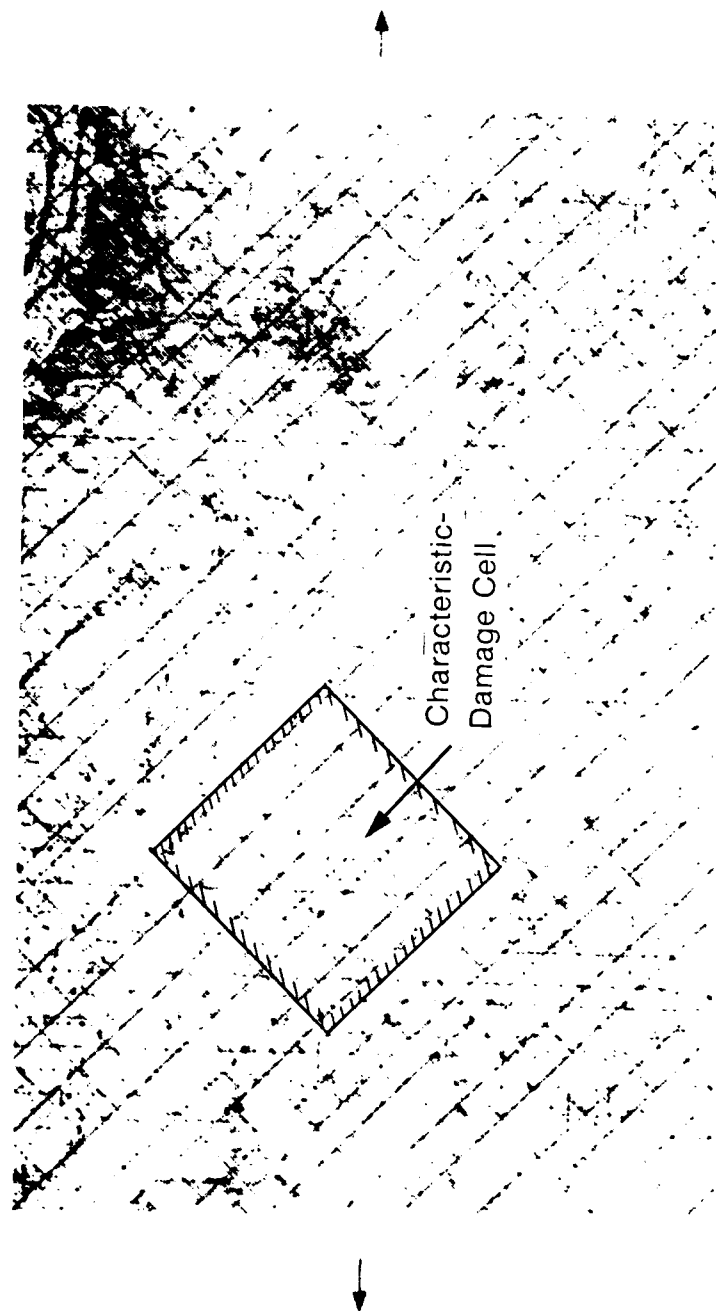


Fig. 1: A radiograph showing the pattern of matrix cracks in a  $[0,90,\pm 45]_s$ , Gr/Ep laminate. (After Highsmith et.al., Ref [26]). The "Characteristic-Damage Cell" is superimposed.

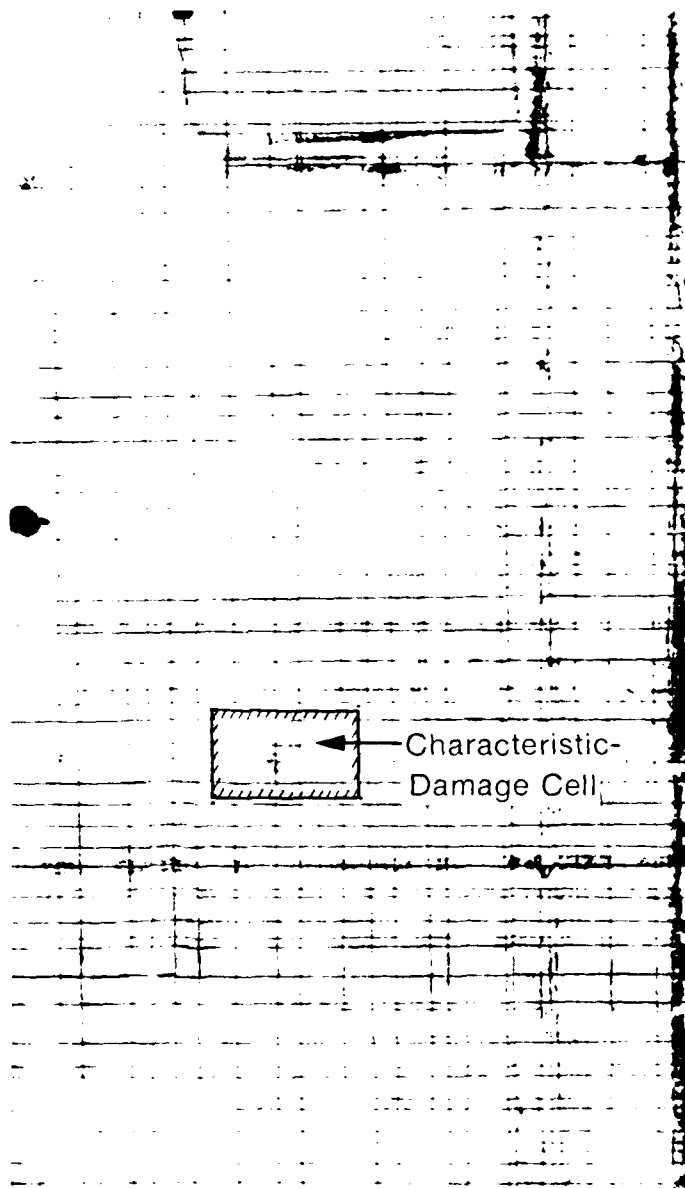


Fig. 2: A radiograph showing the pattern of matrix cracking in a  $[0, 90_2]_5$  Gr/Ep laminate [After Jamison et. al. Ref [25]]. The "Characteristic-Damage Cell" is superimposed.

Finally, it should be noted that each micro-crack is contained within two equal and opposite surfaces. Consequently, the constitutive formulation which employs  $d_{[ij]}$  as an internal state variable should remain insensitive to the sign of  $d_{[ij]}$ .

#### 4. Elastic Response with Distributed Damage.

Consider the response of elastic materials with distributed internal damage. In addition, let the material be exposed to thermal effects and absorb moisture from the ambient environment.

In these circumstances the list of internal state variables contains the deformation gradients  $F_{1J} = \partial x_1 / \partial X_J$ , "damage"  $d_{[ij]}$ , moisture  $m$ , temperature  $T$  and the gradients  $z_i = \partial \mu / \partial x_i$  and  $g_i = \partial T / \partial x_i$  of the chemical potential  $\mu$  and of  $T$ . As noted earlier, both gradients and  $d_{[ij]}$  may be viewed as non-dimensional, while  $F_{1J}$  is obviously dimensionless. In addition,  $T$  and  $\mu$  can be non-dimensionalized as well by dividing their actual values through some reference levels.

Considerations of frame indifference and employment of the reduced entropy inequality [28] give

$$\dot{\rho} = -\rho^* (E_{KL}, D_{[PQ]}, m, T) \quad (3)$$

$$s = -\frac{\dot{\rho}}{\rho T} \quad (9a)$$

$$\dot{m} = -\rho s \frac{\dot{\rho}}{\rho m} \quad (9b)$$

$$S_{KL} = \frac{\rho (s \dot{\rho})}{\dot{E}_{KL}} \quad (9c)$$

and

$$\rho_1 f_1 + \rho_1 (z_1/T + s f_1) + r_{[ij]} \dot{d}_{[ij]} \leq 0 \quad (10)$$

where  $\psi = u - Ts$  is the Helmholtz free energy,  $E_{KL} = \frac{1}{2} (F_{iK} F_{iL} - \delta_{KL})$  are the Lagrangian strain components,  $S_{KL}$  are the components of the symmetric Kirchhoff stress [29],  $D_{[PQ]}$  are the components of the damage variable  $d_{[ij]}$  referred to the undeformed configuration. Since both  $d_{[ij]}$  and  $D_{[PQ]}$  are areas they are related by

$$d_{[ij]} = J X_{L,k} e_{kji} e_{LPQ} D_{[PQ]} \quad (11)$$

with  $J = \det \partial x_i / \partial X_K$ .

In addition, in eqn. (10),  $r_{[ij]}$  is the "affinity" to the rate of damage growth  $\dot{d}_{[ij]} = \dot{d}_{[ij]}$ , namely

$$r_{[ij]} = \psi_s \frac{\dot{d}_{[ij]}}{\dot{d}_{[ij]}} \quad (12)$$

Furthermore, we obtain the following forms for the fluxes

$$Q_A = Q_A^* (E_{KL}, D_{[PQ]}, G_C, Z_B, T, m) \quad (13a)$$

$$F_A = F_A^* (E_{KL}, D_{[PQ]}, G_C, Z_B, T, m) \quad (13b)$$

$$\dot{d}_{[IJ]} = \dot{d}_{[IJ]}^* (E_{KL}, D_{[PQ]}, G_C, Z_B, T, m) \quad (13c)$$

In (13)  $Q_A$ ,  $F_A$ , and  $\dot{d}_{[IJ]}$  are components of heat and moisture flux and of damage growth-rate in the reference coordinates  $X_A$ . They are related to  $q_i$  and  $f_i$  through  $Q_A = X_{A,i} q_i$ ,  $F_A = X_{A,i} f_i$  and  $\dot{d}_{[IJ]}$  is expressible in terms of  $\dot{d}_{[ij]}$  in the same manner as given in eqn. (11) for  $D_{[IJ]}$  and  $d_{[ij]}$ . In addition  $G_C$  and  $Z_B$  are gradients referred to the undeformed configuration, namely  $G_C = x_{i,C} g_i$  and  $Z_B = x_{i,B} z_i$  [7].

To simplify the subsequent formulation we shall restrict ourselves to isothermal conditions. In this case  $g_i = 0$ , whereby

$$F_A = \hat{F}_A (E_{KL}, D_{[PQ]}, Z_B, m; T_0) \quad (14a)$$

and

$$\hat{\psi}_{[IJ]} = \hat{\psi}_{[IJ]}(E_{KL}, D_{[PQ]}, Z_B, m; T_0) \quad (14b)$$

In addition, the inequality (10) reduces to

$$\hat{\mu}_{,i} f_i + r_{[ij]} \hat{\phi}_{[ij]} \leq 0 \quad (15)$$

### 5. Fiber Reinforced Materials. Transverse Isotropy.

Consider uni-directionally reinforced fibrous materials. Such substances are transversely isotropic about, say, the  $x_3$  axis and, in the absence of any right-handed or left-handed internal structure, possess also reflective symmetries in the  $x_1$  and  $x_3$  axes\*.

To derive the detailed dependencies of  $\psi$ ,  $F_A$  and  $\hat{\psi}_{[IJ]}$  on  $E_{KL}$ ,  $D_{[PQ]}$  and  $Z_B$  it is necessary to form all the transversely isotropic invariants among these variables [30].

The complete list is given in the Appendix, where  $A_{ij}$ ,  $W_{ij}$  and  $V_i$  denote a symmetric second rank tensor, a skew-symmetric second rank tensor, and a vector, respectively.

Note that the Appendix lists 33 invariants. However, the thirteen invariants  $I_6, I_{11}, I_{15}, I_{18}, I_{20}, I_{21}, I_{23}, I_{24}, I_{25}, I_{27}, I_{29}, I_{30}, I_{32}$  are odd in  $W_{ij}$  and therefore inadmissible to represent damage that must remain insensitive to the sign of  $d_{[ij]}$ . This leaves 20 invariants for expressing  $F_A$  and  $\hat{\psi}_{[IJ]}$ , as explained in the sequel.

In view of eqn. (8), the free energy  $\psi$  depends only on  $E_{KL}$  and  $D_{[PQ]}$ . Consequently, the scalar  $\psi$  depends only on the ten invariants  $I_1 - I_5, I_9, I_{10}, I_{12}, I_{19}$  and  $I_{22}$ .

\*These combined symmetries are denoted by the class T-4 in reference [30].



Expressions for  $F_A$  are obtained by considering the integrity basis for one symmetric and one skew-symmetric second rank tensor and two vectors under the symmetry T-4, subsequently retaining only those terms which are linear in the second vector [31], [32]. The results of this procedure are listed in the Appendix, where the components of the vector valued function  $\underline{U}$ :  $u_1, u_2, u_3$  are related to those of  $A_{ij}, W_{ij}$  and  $V_i$ . The thirty two terms  $P_1 - P_{23}, H_1 - H_9$  in the expressions for  $(u_1, u_2)$  and  $u_3$  are functions of the 20 invariants  $I_1 - I_5, I_7 - I_{10}, I_{12} - I_{14}, I_{16}, I_{17}, I_{19}, I_{22}, I_{26}, I_{28}, I_{31}$  and  $I_{33}$  formed among  $A_{ij}, W_{ij}$  and  $V_i$ .

In view of the fact that the flux components  $F_A$  must remain insensitive to the sign of the damage variable  $d_{[ij]}$  it is necessary discard all terms odd in  $W_{ij}$ , hence  $P_3 = P_5 = P_8 = P_9 = P_{11} = P_{13} = P_{14} = P_{15} = P_{17} = P_{19} = P_{20} = P_{22} = H_3 = H_5 = H_6 = H_8 = 0$ . This leaves only sixteen terms out of the original lists of 32 terms  $P_1 - P_{23}, H_1 - H_9$ .

Expressions for  $\phi_{[IJ]}$  are obtained by considering the integrity basis for one symmetric second rank tensor, one vector and two skew-symmetric second rank tensors under the symmetry T-4, then retaining only those terms which are linear in the second skew-symmetric tensor. In this manner a list of terms is generated, which contains products of components of  $A_{ij}, W_{ij}$  and  $V_i$  with one component of the second skew-symmetric tensor, say  $Y_{[mn]}$ . At this stage generate a second list of terms by transposing the indices  $m$  and  $n$ , namely by forming scalar components of transposed terms among  $A_{ij}, W_{ij}$  and  $V_i$  that correspond to  $Y_{[nm]}$ .

The desired skew-symmetric tensor valued functions are then obtained by subtracting the factors that multiply  $Y_{[mn]}$  from those which multiply  $Y_{[nm]}$ .

The results of this procedure are given in the Appendix, where  $\chi_{[31]}$ ,  $\chi_{[32]}$  and  $\chi_{[12]}$  are related to components of  $A_{ij}$ ,  $W_{ij}$  and  $V_i$ . The eighteen terms  $r_1 - r_{14}$ ,  $h_1 - h_4$  in the Appendix are functions of the same twenty invariants  $I_1 - I_5$ ,  $I_7 - I_{10}$ ,  $I_{12} - I_{14}$ ,  $I_{16}$ ,  $I_{17}$ ,  $I_{19}$ ,  $I_{22}$ ,  $I_{26}$ ,  $I_{28}$ ,  $I_{31}$  and  $I_{33}$  that enter  $P_1$ ,  $P_2$ , etc. Note that the process of transposition from  $Y_{[mn]}$  to  $Y_{[nm]}$  and subsequent subtraction automatically eliminates all terms odd in  $W_{ij}$  from the list for  $\chi_{[IJ]}$ , hence no further reduction is necessary to account for sign insensitivity to the damage parameter  $d_{[ij]}$ .

#### 6. Infinitesimal Deformations. Strain Formulation.

Consider infinitesimal deformations. In this case  $E_{IJ} \rightarrow \epsilon_{ij}$ ,  $S_{KL} \rightarrow \sigma_{kl}$ ,  $F_I \rightarrow \bar{f}_i$ ,  $D_{[MN]} \rightarrow d_{[mn]}$  and  $\rho_S \approx \rho_{S0}$  (constant).

Expanding the free energy in powers of  $\epsilon_{ij}$ , truncating after the second power, we get

$$\begin{aligned} \phi_{S0} = & \phi_0 + \beta_1 \epsilon_{33} + \beta_2 (\epsilon_{11} + \epsilon_{22}) + \beta_3 [D(\epsilon_{11} - \epsilon_{22}) + 4d_{[31]} d_{[32]} \epsilon_{12}] \\ & + \beta_4 d_{[12]} (\epsilon_{31} d_{[32]} - \epsilon_{32} d_{[31]}) + \gamma_1 \epsilon_{33}^2 + \gamma_2 (\epsilon_{11} + \epsilon_{22})^2 \\ & + \gamma_3 [D(\epsilon_{11} - \epsilon_{22}) + 4d_{[31]} d_{[32]} \epsilon_{12}]^2 \\ & + \gamma_4 d_{[12]}^2 (\epsilon_{31} d_{[32]} - \epsilon_{32} d_{[31]})^2 + \gamma_5 \epsilon_{33} (\epsilon_{11} + \epsilon_{22}) \\ & + \gamma_6 \epsilon_{33} [D(\epsilon_{11} - \epsilon_{22}) + 4d_{[31]} d_{[32]} \epsilon_{12}] \\ & + \gamma_7 \epsilon_{33} d_{[12]} (\epsilon_{31} d_{[32]} - \epsilon_{32} d_{[31]}) \\ & + \gamma_8 (\epsilon_{11} + \epsilon_{22}) [D(\epsilon_{11} - \epsilon_{22}) + 4d_{[31]} d_{[32]} \epsilon_{12}] \\ & + \gamma_9 (\epsilon_{11} + \epsilon_{22}) d_{[12]} (\epsilon_{31} d_{[32]} - \epsilon_{32} d_{[31]}) \end{aligned}$$

$$\begin{aligned}
& + \gamma_{10} [D(\epsilon_{11} - \epsilon_{22}) + 4d_{[31]}d_{[32]}\epsilon_{12}]d_{[12]}(\epsilon_{31}d_{[32]} - \epsilon_{32}d_{[31]}) \\
& + \gamma_{11} [(\epsilon_{11} - \epsilon_{22})^2 + 4\epsilon_{12}^2] + \gamma_{12} (\epsilon_{31}^2 + \epsilon_{32}^2) \\
& + \gamma_{13}d_{[12]} [(\epsilon_{11} - \epsilon_{22})(\epsilon_{31}d_{[32]} + \epsilon_{32}d_{[31]}) - 2\epsilon_{12}(\epsilon_{31}d_{[31]} - \\
& \quad \epsilon_{32}d_{[32]})] \quad (16)
\end{aligned}$$

where  $\gamma_0, \beta_i$  ( $i = 1, \dots, 4$ ),  $\gamma_i$  ( $i = 1, \dots, 13$ ) are functions of  $m, d_{[31]}^2 + d_{[32]}^2, d_{[12]}^2$ , and  $T_0$ . Also  $D = d_{[31]}^2 - d_{[32]}^2$ .

Stress-strain relations are obtainable from  $\sigma_{ij} = \rho_{so} \frac{\partial \psi}{\partial \epsilon_{ij}}$ , where  $\epsilon_{ij}$  is considered independent of  $\sigma_{ji}$ . This requires to reconsider the expansion (16), which is "biased" in favor of  $\epsilon_{12}, \epsilon_{31}$  and  $\epsilon_{32}$  and replace those shear strains by  $\frac{1}{2}(\epsilon_{ij} + \epsilon_{ji})$ . Upon performing this modification, and then employing the "truncated" notation, with  $\sigma_{11} \rightarrow \sigma_1, \sigma_{22} \rightarrow \sigma_2, \sigma_{33} \rightarrow \sigma_3, \sigma_{23} \rightarrow \sigma_4, \sigma_{31} \rightarrow \sigma_5, \sigma_{12} \rightarrow \sigma_6$  and  $\epsilon_{11} \rightarrow \epsilon_1, \epsilon_{22} \rightarrow \epsilon_2, \epsilon_{33} \rightarrow \epsilon_3, 2\epsilon_{23} \rightarrow \epsilon_4, 2\epsilon_{31} \rightarrow \epsilon_5$ , and  $2\epsilon_{12} \rightarrow \epsilon_6$ , we obtain

$$\sigma_p = C_{p0} + C_{pq}\epsilon_q \quad \text{where} \quad C_{pq} = C_{qp} \quad (17)$$

In (17), we have

$$C_{10} = \beta_2 + \beta_3 D, \quad C_{20} = \beta_2 - \beta_3 D, \quad C_{30} = \beta_1,$$

$$C_{40} = -\frac{1}{2}\beta_4 d_{[12]}d_{[31]}, \quad C_{50} = \frac{1}{2}\beta_4 d_{[12]}d_{[32]}$$

$$C_{60} = 2\beta_3 d_{[31]}d_{[32]}$$

and

$$C_{11} = 2(\gamma_2 + \beta_3 D^2 + \beta_3 D + \gamma_{11}), \quad C_{12} = 2(\gamma_2 - \beta_3 D^2 - \gamma_{11}),$$

$$C_{13} = \gamma_5 + \gamma_6 D, \quad C_{14} = \frac{1}{2}(-\gamma_9 - \gamma_{10} D + \gamma_{13})d_{[12]}d_{[31]},$$

$$C_{15} = \frac{1}{2}(\gamma_9 + \gamma_{10} D + \gamma_{13})d_{[12]}d_{[32]},$$

$$C_{16} = 2(2\beta_3 D + \beta_3)d_{[31]}d_{[32]},$$

$$\begin{aligned}
C_{22} &= 2(\gamma_2 + \gamma_3 D^2 - \gamma_3 D + \gamma_{11}), & C_{23} &= \gamma_5 - \gamma_6 D, \\
C_{24} &= \frac{1}{2}(-\gamma_9 + \gamma_{10} D - \gamma_{13}) d_{[12]} d_{[31]}, \\
C_{25} &= \frac{1}{2}(\gamma_9 - \gamma_{10} D - \gamma_{13}) d_{[12]} d_{[32]}, \\
C_{26} &= 2(-2\gamma_3 D + \gamma_8) d_{[31]} d_{[32]}, & C_{33} &= 2\gamma_1, & C_{34} &= -\frac{\gamma_7}{2} d_{[12]} d_{[31]}, \\
C_{35} &= \frac{\gamma_7}{2} d_{[12]} d_{[32]}, & C_{36} &= 2\gamma_6 d_{[31]} d_{[32]}, \\
C_{44} &= \gamma_4 d_{[12]}^2 d_{[31]}^2 + \frac{1}{2} \gamma_{12}, & C_{45} &= -\gamma_4 d_{[12]}^2 d_{[31]} d_{[32]}, \\
C_{46} &= -\gamma_{10} d_{[31]}^2 d_{[32]} d_{[12]} + \frac{\gamma_{13}}{2} d_{[12]} d_{[32]}, \\
C_{55} &= \gamma_4 d_{[12]}^2 d_{[32]}^2 + \frac{\gamma_{12}}{2}, & C_{56} &= (\gamma_{10} d_{[32]}^2 - \frac{\gamma_{13}}{2}) d_{[12]} d_{[31]}, \\
C_{66} &= 2(4\gamma_3 d_{[31]}^2 d_{[32]}^2 + \gamma_{11})
\end{aligned}$$

Note that when all  $d_{[ij]}$  vanish the stress-strain relations reduce to the familiar expressions for transverse isotropy about the  $x_3$  axis. However, in the presence of damage the stiffness matrix  $C_{pq}$  contains all 21 components, all of which depend on  $d_{[ij]}$ . Obviously, all stiffness components may depend also on  $m$  and  $T_0$ .

For  $\epsilon_{ij} \ll 1$  we neglect all terms that involve the symmetric second rank tensor in the Appendix and obtain the following expressions for the vector that represents the moisture flux  $\underline{f}$ :

$$\begin{aligned}
f_1 &= P_1 z_1 + P_6 [(d_{[31]}^2 - d_{[32]}^2) z_1 + 2d_{[31]} d_{[32]} z_2] \\
f_2 &= P_1 z_2 + P_6 [-(d_{[31]}^2 - d_{[32]}^2) z_2 + 2d_{[31]} d_{[32]} z_1] \\
f_3 &= H_1 z_3 + H_7 d_{[12]} (d_{[31]} z_2 - d_{[32]} z_1)
\end{aligned} \tag{18}$$

In (18)  $P_1$ ,  $P_6$ ,  $H_1$  and  $H_7$  are functions of the twenty invariants  $I_1 - I_5$ ,  $I_7 - I_{10}$ ,  $I_{12} - I_{14}$ ,  $I_{16}$ ,  $I_{17}$ ,  $I_{19}$ ,  $I_{22}$ ,  $I_{26}$ ,  $I_{28}$ ,  $I_{31}$  and  $I_{33}$  formed from the components of the symmetric tensor  $\epsilon_{ij}$ , the skew-symmetric tensor  $d_{[ij]}$  and the vector  $z_i$ . Obviously  $P_1$ ,  $P_6$ ,  $H_1$  and  $H_7$  may depend also on the  $m$  and on the (constant) temperature  $T_0$ . Note that the expansion of  $\psi$  in power

series of  $\phi_{ij}$  does NOT imply that an analogous expansion must exist for  $P_1$ ,  $P_6$ ,  $H_1$  and  $H_7$ . The present formulation therefore retains the option to consider non-linear coupling between mechanical fields and moisture flux [33].

Finally, employing similar arguments, we obtain the following expressions for the damage growth rates  $\dot{\phi}_{[ij]} = \dot{d}_{[ij]}$ :

$$\begin{aligned}\dot{\phi}_{[12]} &= h_1 d_{[12]} + h_4 (d_{[31]} z_2 - d_{[32]} z_1) z_3 \\ \dot{\phi}_{[31]} &= r_1 d_{[31]} + r_4 [(z_1^2 - z_2^2) d_{[31]} + z_2 (z_1 d_{[32]} - z_3 d_{[12]})] \\ &\quad + r_{11} d_{[12]} d_{[31]} z_1 z_2 + r_{13} (d_{[12]} z_3 - d_{[32]} z_1) z_2 \\ \dot{\phi}_{[32]} &= r_1 d_{[32]} + r_4 [-(z_1^2 - z_2^2) d_{[32]} + z_1 (z_2 d_{[31]} - z_3 d_{[12]})] \\ &\quad - r_{11} d_{[12]} d_{[32]} z_1 z_2 - r_{13} (d_{[12]} z_3 - d_{[13]} z_2) z_1\end{aligned}\quad (19)$$

In (19), the terms  $h_1$ ,  $h_4$ ,  $r_1$ ,  $r_4$ ,  $r_{11}$  and  $r_{13}$  are functions of the same invariants as  $P_1$ ,  $P_6$ ,  $H_1$ , and  $H_7$  above. Note that the terms  $h_1$  and  $r_1$  correspond to "self similar" damage growth, while the remaining functions  $h_4$ ,  $r_4$ ,  $r_{11}$  and  $r_{13}$  are associated with the "tilting" of micro-damage due to gradients of the chemical potential.

## 7. Infinitesimal Deformation. Stress Formulation.

Define the Gibbs free energy  $\phi(\sigma_{ij}, d_{[ij]}, m; T_0)$  by

$$\phi_{so}^t = \phi_{so}^0 - \sigma_{ij} \epsilon_{ij} \quad (20)$$

Then, in analogy with eqns. (9) we have

$$\epsilon_{ij} = \phi_{so} \frac{\partial \phi}{\partial \sigma_{ij}} \quad (21a)$$

$$s = - \frac{\partial \phi}{\partial T} \quad (21b)$$

$$L = \phi_{so} \frac{\partial \phi}{\partial m} \quad (22b)$$

The "reduced entropy inequality", eqn. (10), remains unchanged, except that now

$$\epsilon_{[ij]} = \epsilon_{so} \frac{\sigma_{ij}}{\sigma_f} \quad (23)$$

Consider a characteristic material stress, e.g. a failure stress  $\sigma_f$ , then for sufficiently small stresses (such that  $\sigma_{ij}/\sigma_f \ll 1$ ) we can expand  $\epsilon$  in powers of  $\sigma_{ij}$  and truncate after the second powers. This expansion has the same form as eqn. (16), except that  $\sigma_{ij}$  replaces  $\epsilon_{ij}$ , expansional coefficients  $(-B_i)$  replace  $\beta_i$ , and compliances  $(-\eta_i)$  replace the stiffnesses  $\gamma_i$ . An analogous procedure yields linear strain-stress relations similar to those given in eqn. (17)

$$\epsilon_p = S_{p0} + S_{pq}\sigma_q \quad (24)$$

with  $S_{p0}$  and  $S_{pq}$  the same as  $C_{p0}$  and  $C_{pq}$  except that  $B_i$  and  $\eta_i$  appear in place of  $\beta_i$  and  $\gamma_i$ . In addition, expressions (13) and (19) also remain unchanged, except that  $P_1, P_6, H_1, H_7, h_1, h_4, r_1, r_4, r_{11}$  and  $r_{13}$  depend on twenty invariants that contain  $\sigma_{ij}$  in place of  $\epsilon_{ij}$ .

In view of (22b), the chemical potential  $\tilde{\mu}$  is given by

$$\begin{aligned} \tilde{\mu} = \epsilon_{so} \frac{\sigma}{\sigma_f} = & \frac{\sigma}{\sigma_f} \left[ \frac{\partial \epsilon_{so}}{\partial \sigma} - \frac{\partial B_1}{\partial \sigma} \left( \frac{\sigma_{33}}{\sigma_f} \right) - \frac{\partial B_2}{\partial \sigma} \left( \frac{\sigma_{11} + \sigma_{22}}{\sigma_f} \right) \right. \\ & - \frac{\partial B_3}{\partial \sigma} \left[ 0 \left( \frac{\sigma_{11} - \sigma_{22}}{\sigma_f} \right) + 4 d_{[31]} d_{[32]} \left( \frac{\sigma_{12}}{\sigma_f} \right) \right] \\ & - \frac{\partial B_4}{\partial \sigma} d_{[12]} \left[ d_{[32]} \left( \frac{\sigma_{31}}{\sigma_f} \right) - d_{[31]} \left( \frac{\sigma_{32}}{\sigma_f} \right) \right] \\ & \left. + \text{higher order terms in } (\sigma_{ij}/\sigma_f) \right] \quad (25) \end{aligned}$$

For constant stresses the fluxes  $z_i = -\sigma_i/x_i$  are given by

$$\begin{aligned} z_i = -\sigma_{so} \left[ \frac{\partial^2 \epsilon_{so}}{\partial \sigma^2} \frac{\sigma}{x_i} + 2 \frac{\partial^2 \epsilon_{so}}{\partial \sigma \partial \sigma_{[31]} + \partial \sigma_{[32]}} \left( d_{[31]} \frac{\sigma_{[31]}}{x_i} + d_{[32]} \frac{\sigma_{[32]}}{x_i} \right) \right. \\ \left. + 2 \frac{\partial^2 \epsilon_{so}}{\partial \sigma \partial d_{[12]}} d_{[12]} \frac{\sigma_{[12]}}{x_i} \right] \quad (26) \end{aligned}$$

In view of (25),  $z_i$  will depend on  $\frac{\sigma_o^2}{\sigma_m^2}$ ,  $\frac{\sigma_o^2}{\sigma_m^2(d_{[31]}^2 + d_{[32]}^2)}$ ,  $\frac{\sigma_o^2}{\sigma_m^2 d_{[12]}^2}$ , and on  $\frac{\sigma_{B_i}^2}{\sigma_m^2}$ ,  $\frac{\sigma_{B_i}^2}{\sigma_m^2(d_{[31]}^2 + d_{[32]}^2)}$ ,  $\frac{\sigma_{B_i}^2}{\sigma_m^2 d_{[12]}^2}$

( $i=1, \dots, 4$ ) as well as on terms like  $\frac{\sigma_{B_3}}{\sigma_m} \frac{\sigma_D}{\sigma_{x_i}}$ . In view of the dependence of  $P_1, P_6, \dots, r_{13}$  in eqns. (19) on  $\sigma_{ij}$  it follows that  $d_{[ij]}$  may introduce a non-linear stress effect on  $z_i$ . However, for sufficiently short times - when  $d_{[ij]}$  remain relatively small - it is plausible to expect that for  $\sigma_{ij}/\sigma_f \ll 1$   $z_i$  will be linear in  $\sigma_{ij}$ .

### 3. A Special Sub Case: Unidirectional Diffusion Under a Constant Transverse Load.

Consider a unidirectionally reinforced plate of thickness  $h$ , with fibers parallel to the  $x_3$  axis, subjected to a constant stress  $\sigma_{22} = \sigma_0$  with diffusion in the  $x_1$  direction, as sketched in Fig. 3.

In view of the observation that most damage due to moisture occurs at the fiber-matrix interfaces \*[9],[16],[17],[34] assume  $d_{[12]} = 0$ . Furthermore, assume gradients only in the  $x_1$  direction. Then,

by (26),  $z_2 = z_3 = 0$ .

In these circumstances eqn. (24) gives

$$\epsilon_i = S_{i0} + S_{i2}\sigma_0 \quad (i = 1, 2, 3, 6), \quad \text{while } \epsilon_4 = \epsilon_5 = 0.$$

In addition, eqns. (18), (19), (25) and (26) yield:

damage growth rates:

$$\dot{d}_{[32]} = r_1 \dot{d}_{[32]} - r_4 z_1^2 \dot{d}_{[32]} \quad (27a)$$

$$\dot{d}_{[31]} = r_1 \dot{d}_{[31]} + r_4 z_1^2 \dot{d}_{[31]} \quad (27b)$$

moisture fluxes:

$$f_1 = P_1 z_1 + P_6 D z_1 \quad (28a)$$

$$f_2 = 2P_6 d_{[31]} d_{[32]} z_1 \quad (28b)$$

chemical potential and its gradient

$$\mu = \frac{\mu_0}{m} - \frac{B_2}{m} \left( \frac{\sigma}{f} \right) + \frac{B_3}{m} D \left( \frac{\sigma}{f} \right) + O((\sigma/\sigma_f)^2) \quad (29a)$$

$$z_i = R_1 \frac{\mu}{x_i} + R_2 \frac{\partial \mu}{\partial x_1} + R_3 \frac{\partial (d_{[31]}^2 + d_{[32]}^2)}{\partial x_1} + O((\sigma/\sigma_f)^2) \quad (29b)$$

where

$$R_1 = \frac{B_2}{m^2} - \frac{B_2}{m^2} \left( \frac{\sigma}{f} \right) + \frac{B_3}{m^2} D \left( \frac{\sigma}{f} \right), \quad R_2 = \frac{B_3}{m} \left( \frac{\sigma}{f} \right),$$

$$R_3 = \frac{B_2}{m (d_{[31]}^2 + d_{[32]}^2)} - \frac{B_2}{m (d_{[31]}^2 + d_{[32]}^2)} \left( \frac{\sigma}{f} \right) + \frac{B_3}{m (d_{[31]}^2 + d_{[32]}^2)} D \left( \frac{\sigma}{f} \right)$$

\*See also Fig. 8 below.



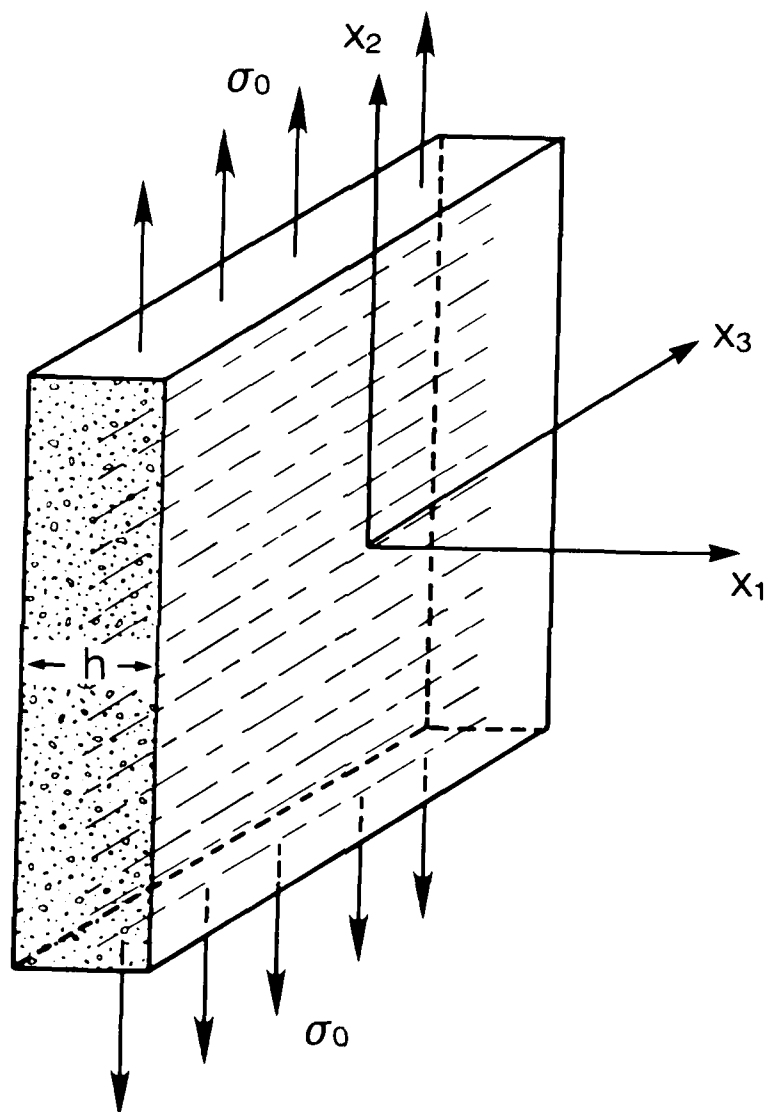


Fig. 3: The geometry of a uni-directionally reinforced coupon, with fibers in the  $x_3$ -direction, diffusion in the  $x_1$ -direction and load in the  $x_2$ -direction

In the present circumstances  $r_1$ ,  $r_4$ ,  $P_1$ , and  $P_6$  in eqns. (27) and (28) depend on the following six terms:  $\left\{ \phi_0, d_{[31]}^2 + d_{[32]}^2, z_1^2, \phi_0 D, \phi_0 z_1^2, z_1^2 D \right\}$  as well as on  $m$ . The quantities  $\phi_0$ ,  $B_2$ , and  $B_3$  in (29a) depend on  $d_{[31]}^2 + d_{[32]}^2$  and on  $m$ .

In (28), (29) and the above  $D = d_{[31]}^2 - d_{[32]}^2$  as before.

In view of (28) and (29b) the process of moisture transport involves a moisture, stress and damage affected diffusivity. Perhaps more significantly, the terms  $(d_{[31]}^2 + d_{[32]}^2)/x_1$  and  $\partial D/\partial x_1$  in (29b) indicate that sorption is influenced by damage gradients which "channel" moisture in the direction of increasing damage. Eqns. (29) indicate that  $\tilde{u}$  depends linearly on stress and that such linear dependence is likely to occur also for the diffusivity, at least for early stages of damage development.

The boundary condition on moisture content is determined by

$$\tilde{u}(x_1 = \pm \frac{h}{2}, t) = \mu_A \quad (30)$$

where  $\mu_A$  is the chemical potential of the ambient vapor. For small concentration levels it is plausible to assume that  $\tilde{u}$  is linearly related to  $m$ , whereby (29a) predicts saturation levels which, at least for early stages of damage growth, depend linearly on the stress  $\sigma_0$ .

An experimental investigation of stress-assisted diffusion in AS4/3502 graphite/epoxy coupons was concluded recently [35]. Unidirectionally reinforced specimens were exposed to a constant relative humidity of 97%, at a temperature of 40°C, and loaded transversely to the fiber directions at 0%, 15%, 30%, and 45% of the ultimate stress (where  $\sigma_f$  7500 psi = 51.7 MPa). Total moisture weight-gains were recorded periodically in several replicate specimens and results for the average values are shown in Fig. 4 below. Note the "sigmoidal" shape of all absorption curves, which differs qualitatively from predictions of classical diffusion and indicates a non-

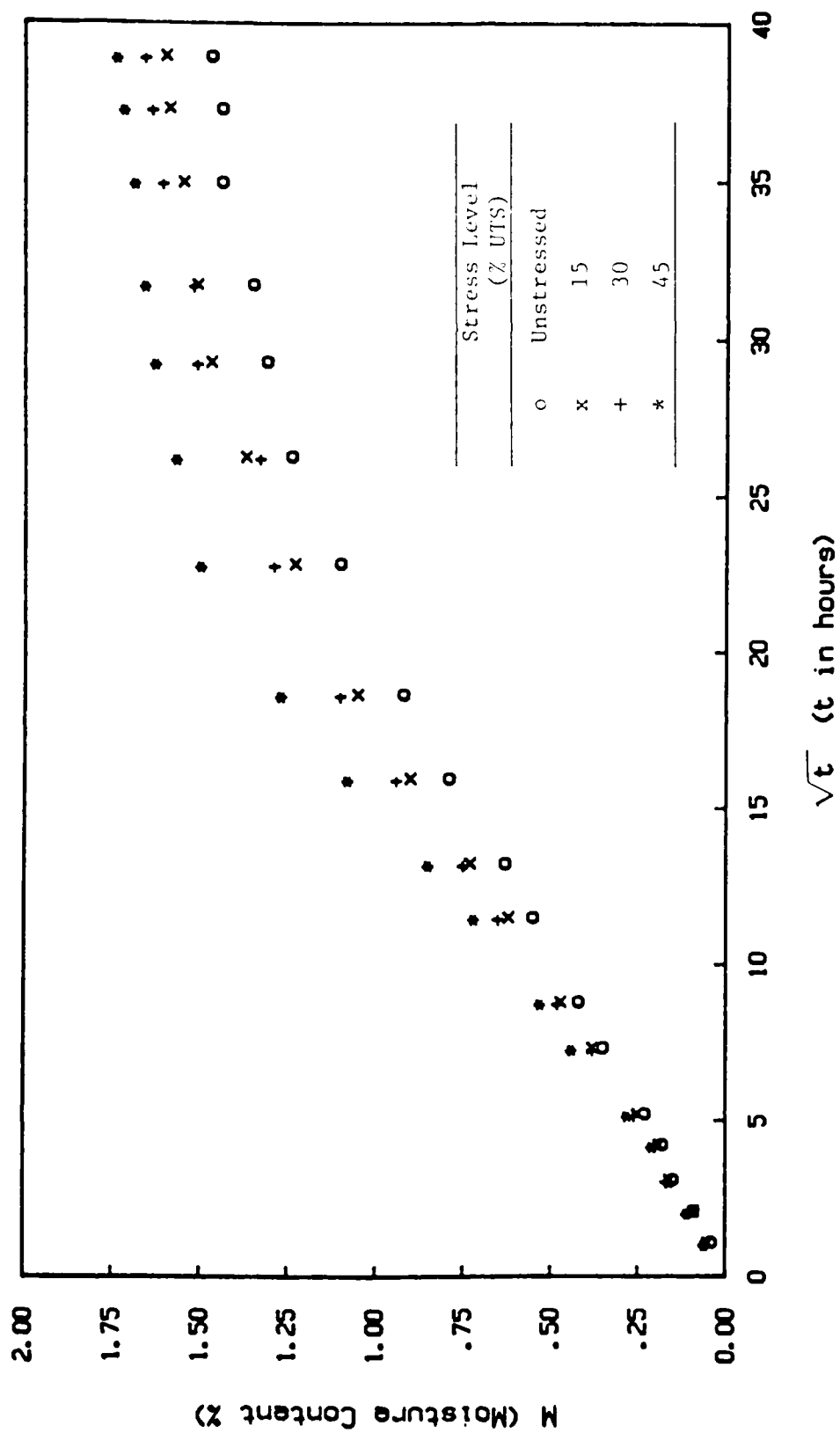


Figure 4. Average moisture content as a function of  $\sqrt{\text{time}}$  in AS4/3502 graphite epoxy coupons subjected to various stress levels during absorption (97% RH and 40°C).

linear, concentration dependent transport process.

The dependence of the maximal moisture content and of the diffusivity on stress are shown in Figs. 5 and 6. It can be seen that an approximately linear relationship exists between stress and both of the above quantities, as inferred by the present model.

Moisture weight-losses were measured during desorption at all the abovementioned stress levels. These measurements were performed after removing all test coupons from the humid chambers into a dry environment at 0% relative humidity. The resulting weight losses are plotted vs.  $\sqrt{t}$  in Fig. 7, where the weight-gain data are superimposed for each stress level for purpose of comparison. Note the substantial hysteresis loops, which can be attributed either to the concentration dependence of the transport process or to the growth of damage, or to both.

#### 9. Moisture Induced Damage In The Absence Of External Stress.

Consider an unstressed unidirectionally reinforced plate, of thickness  $h$  as before with all fibers parallel to the  $x_3$  axis and moisture diffusion in the  $x_1$  direction. In this case eqns. (27) and (28) remain unchanged, except that  $r_1$ ,  $r_4$ ,  $p_1$  and  $p_6$  depend only on  $d_{[31]}^2 + d_{[32]}^2$ ,  $z_1$  and  $m$ .

Eqns. (29) reduce to

$$\frac{\partial^2 c}{\partial x_1^2} = \frac{\partial^2 c}{\partial x_1^2} \quad (31a)$$

and

$$z_1 = \frac{\partial^2 c}{\partial x_1^2} \frac{m}{2} + \frac{\partial^2 c}{\partial x_1^2} \frac{m(d_{[31]}^2 + d_{[32]}^2)}{2} \quad (31b)$$

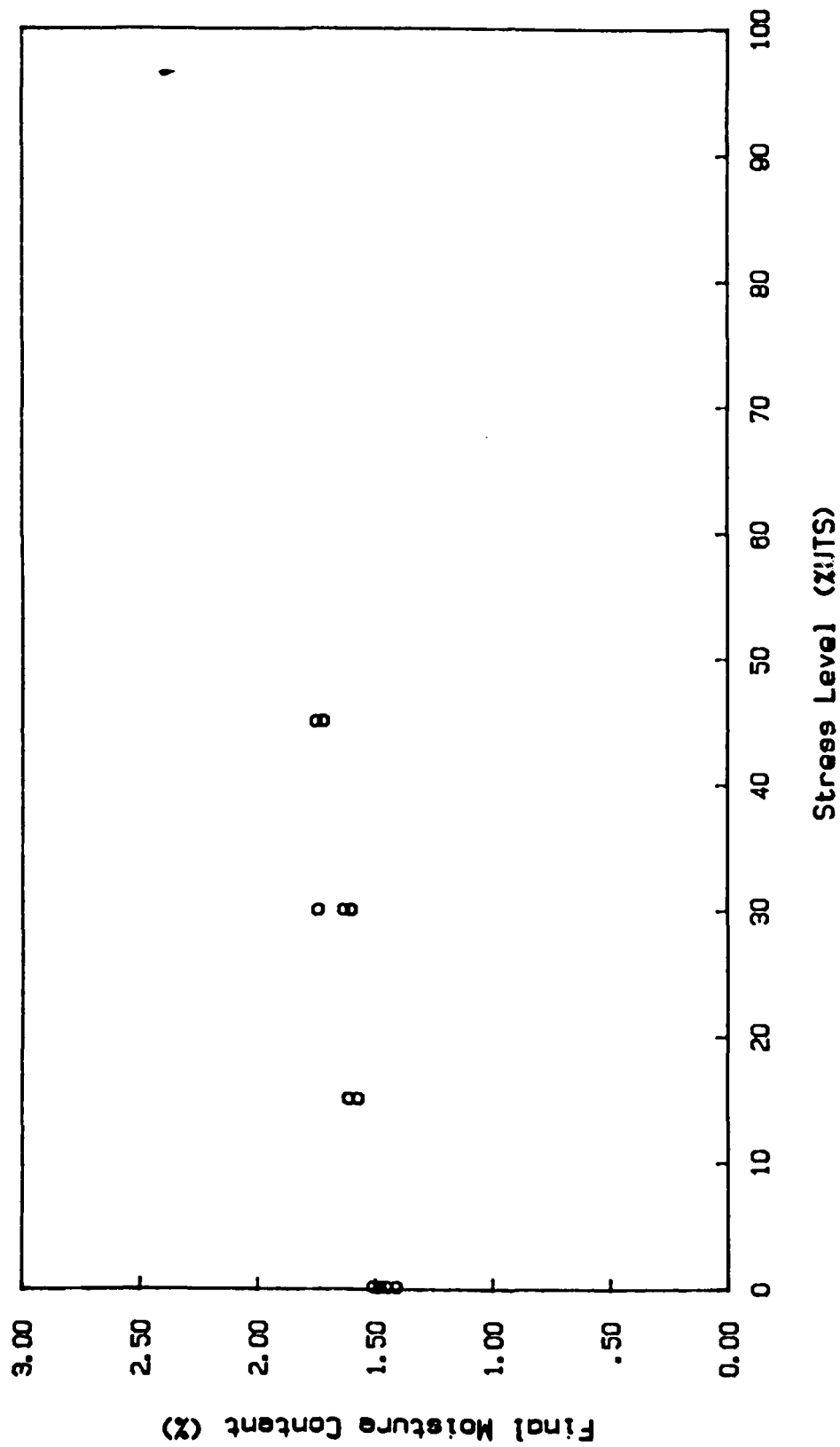


Figure 5. Maximum moisture content obtained in absorption as a function of the applied stress for AS4/3502 graphite epoxy coupons.

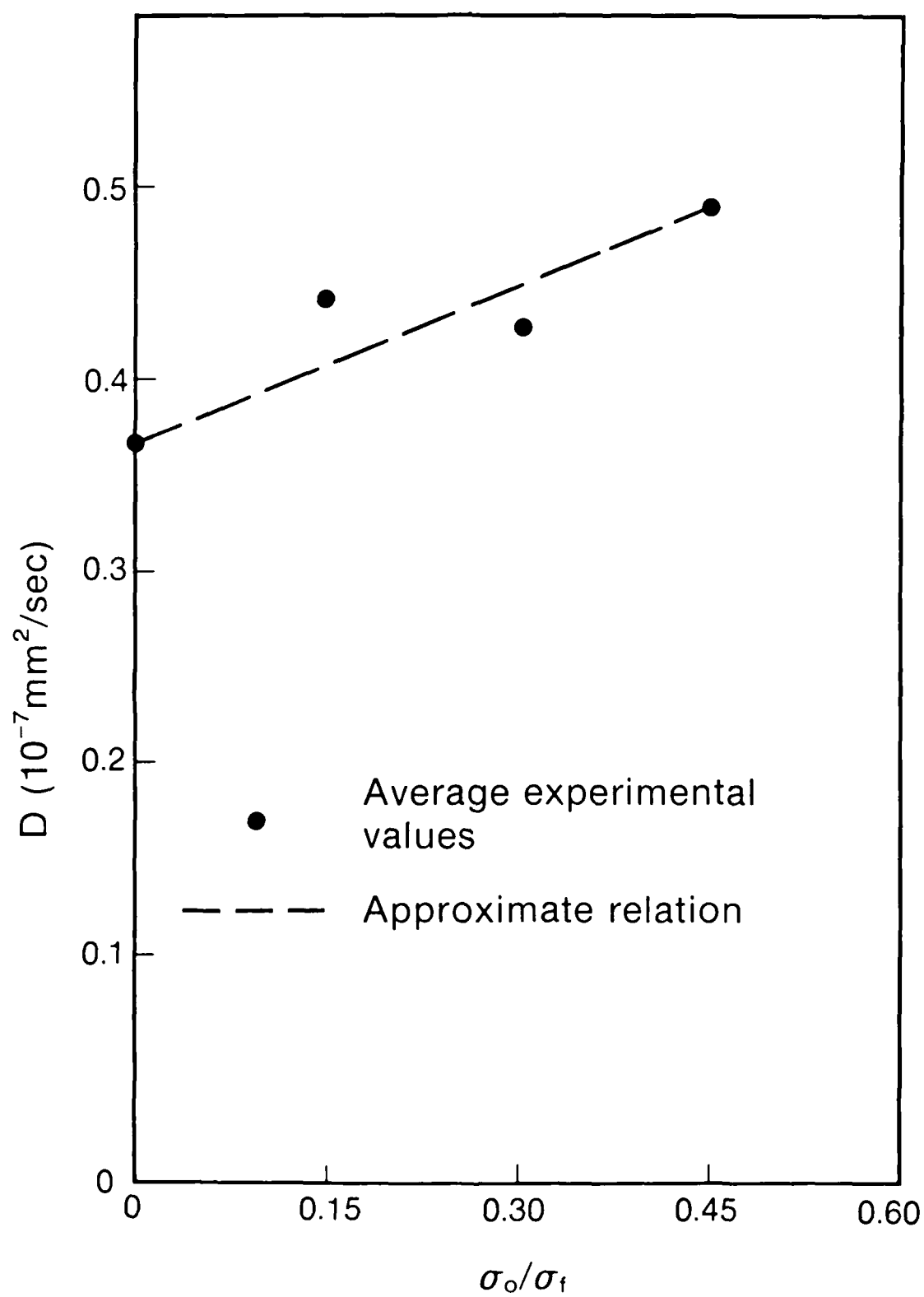


Fig. 6: Variation of the "Equivalent Fickian" Moisture-Diffusivity Coefficient  $D$  with stress.

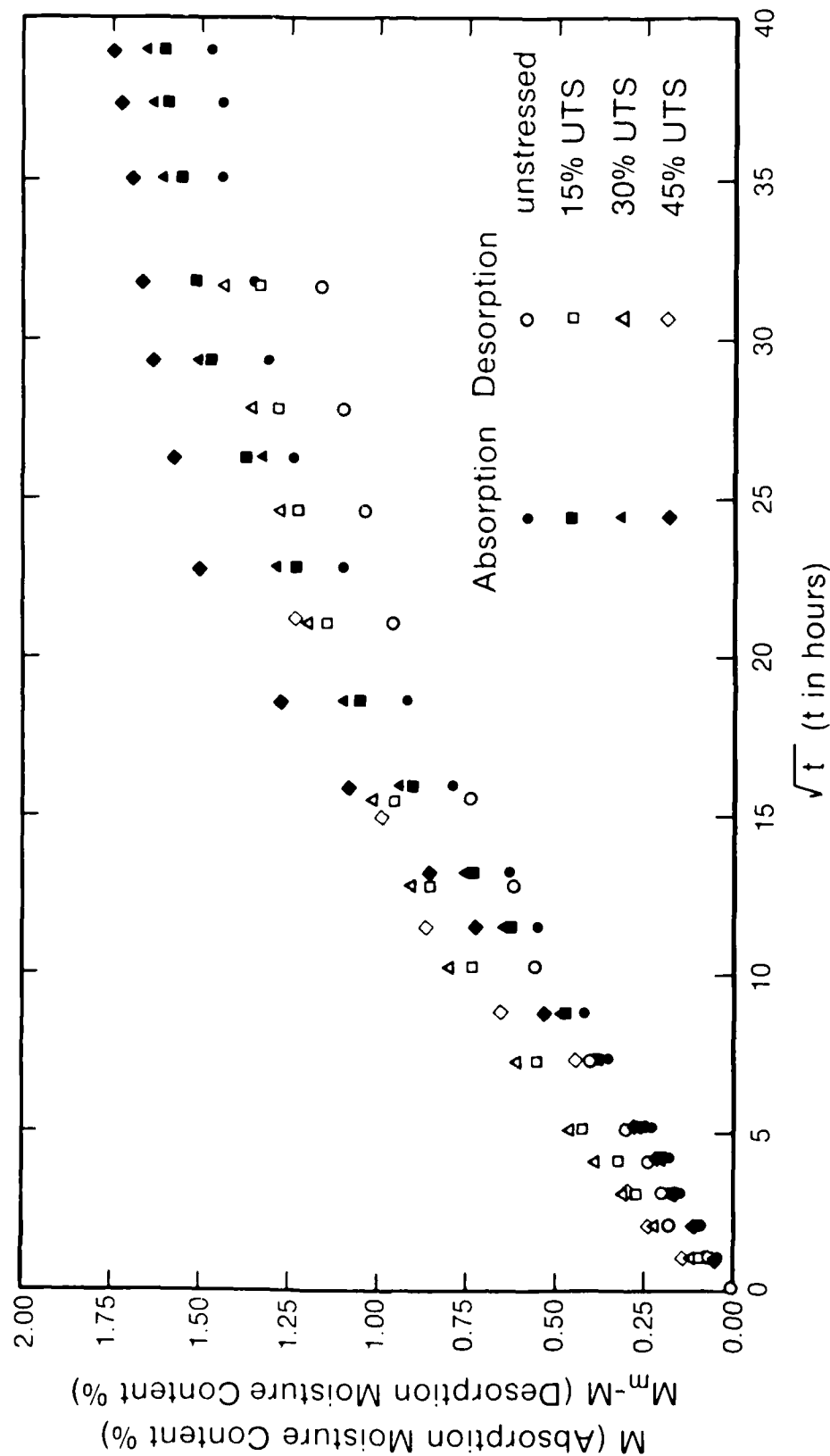


Fig. 7: Superimposed values of moisture content  $M$  during absorption and  $M - M_m$  during desorption ( $M_m$  is max. absorbed content) vs.  $\sqrt{t}$  in unidirectional AS4/3502 Gr/Ep coupons showing the hysteresis loops at various stress levels. Loads applied transversely to fiber direction. Absorption at 97% R.H., desorption at 0% R.H. (All tests at temperature of 40°C).

In view of eqns. (27) and (31b) it is clear that damage growth rate depends on the extent of existing damage and that this rate may also depend on moisture content and the magnitude of the moisture gradient. A dependence of  $\dot{d}_{[ij]}$  on  $d_{[ij]}$  would lead to a synergistic effect which accentuates damage localization ("damage breeds upon itself"). A dependence of  $\dot{d}_{[ij]}$  upon  $|\partial m / \partial x_i|$  would tend to localize the damage in places of highest moisture gradients, namely near the boundaries  $x_1 = \pm h/2$ .

The typical form of moisture induced damage is shown in Fig. 8. Note that "damage" occurs as debondings at the fiber/matrix interfaces. Initially, those debondings appear as isolated interfacial crescents. Upon repeated absorption/desorption cycles these crescents grow, until they coalesce to create highly localized damage in the form of continuous cracks. Typical forms of such cracks are shown in Figs. 9 and 10.

The growth of damage can be inferred also from weight-gain and curvature measurements in anti-symmetric, cross-ply composite plates<sup>[17]</sup>,<sup>[36]</sup>. Due to the anti-symmetry of the lay-up, those plates deform into saddle shaped surfaces upon cool-down from the elevated cure temperature, with initial curvatures  $k_x = -k_y = k_1$ . Upon subsequent exposure to moisture, those curvatures vary with time, whereby  $k=k(t)$ . The variation of  $k_1 - k(t)$  vs. time is shown in Figs. 11 and 12, where experimental results are compared against theoretical predictions of linear elasticity and linear viscoelasticity. (In those figures  $h$  denotes plate thickness and in Fig. 11  $t_g$  denotes time required to saturate initially dry plates, prior to their exposure to cyclic ambient humidities).

The variation of the total moisture content  $M$  vs. time in the anti-symmetric cross-ply plates is shown in Figs. 13 and 14. Weight-gain data points are shown in comparison with predictions of classical diffusion



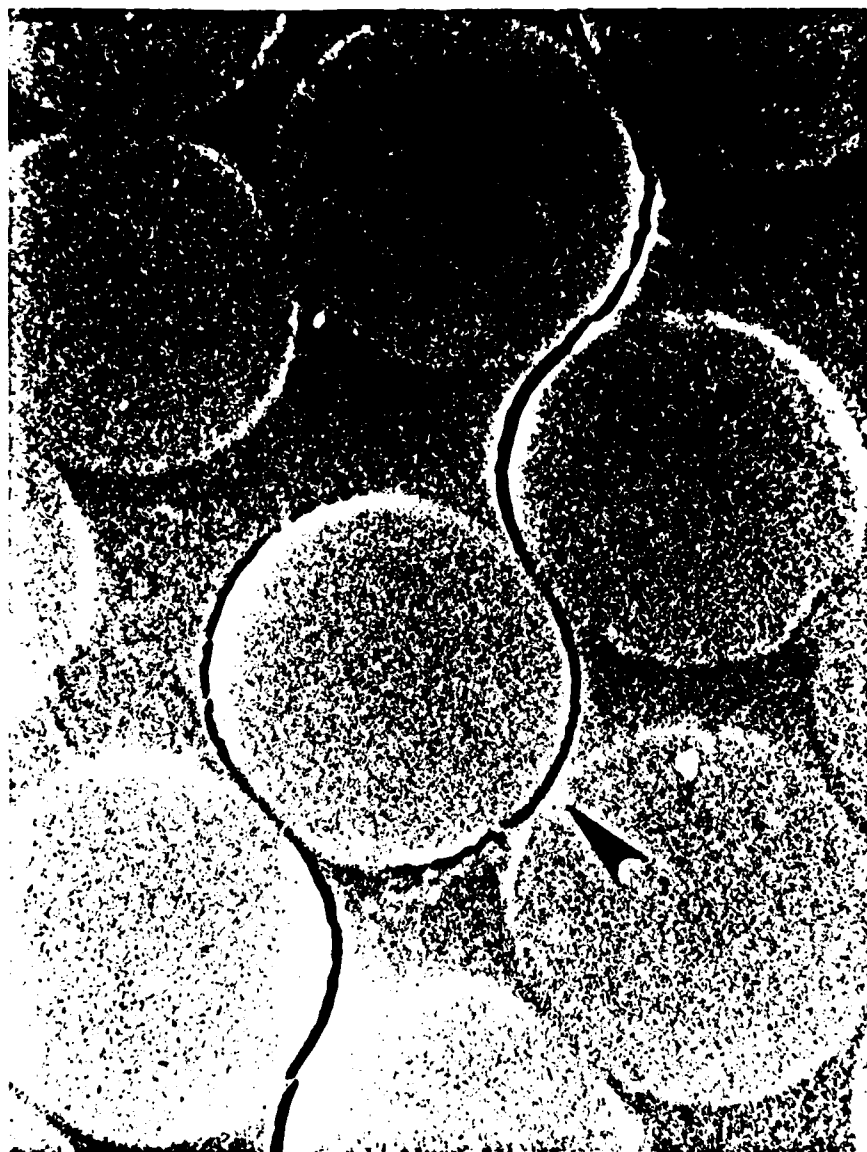


FIG. 8: A scanning electron microscope photo, showing typical debondings at the fiber/matrix interfaces due to moisture in AS4/3502 Gr/Ep composite.

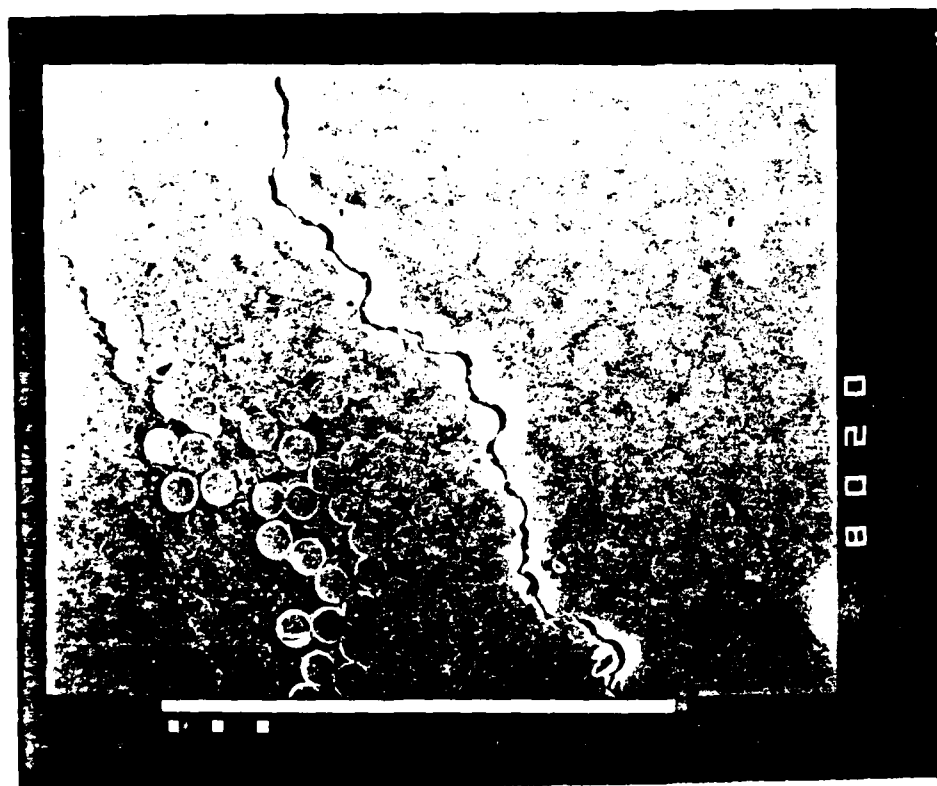


Fig. 10: Microcrack coalescence in an initially dry, unidirectional AS4/3502, Gr/Ep laminate exposed to 9 cycles of 0% and 95% R.H. at 24-day intervals.

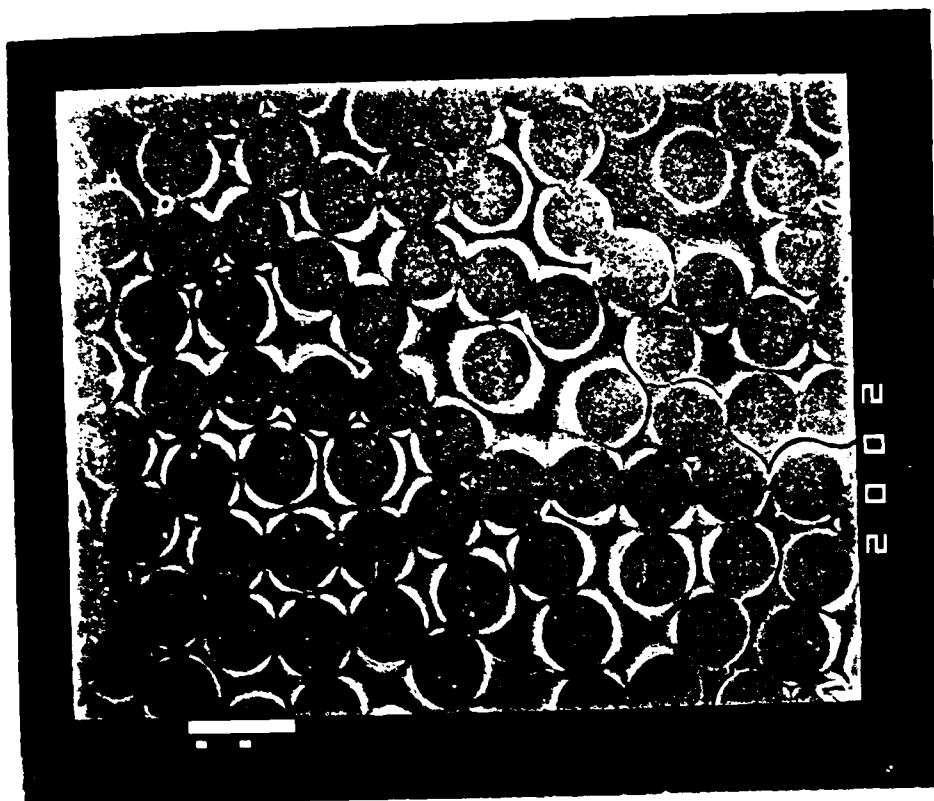


Fig. 9: Profuse microcracking, with some crack coalescence in an initially saturated, unidirectional AS4/3502, Gr/Ep laminate exposed to three cycles of 65% and 95% R.H. at 24-day intervals. Photo taken after the third exposure to 65% R.H.

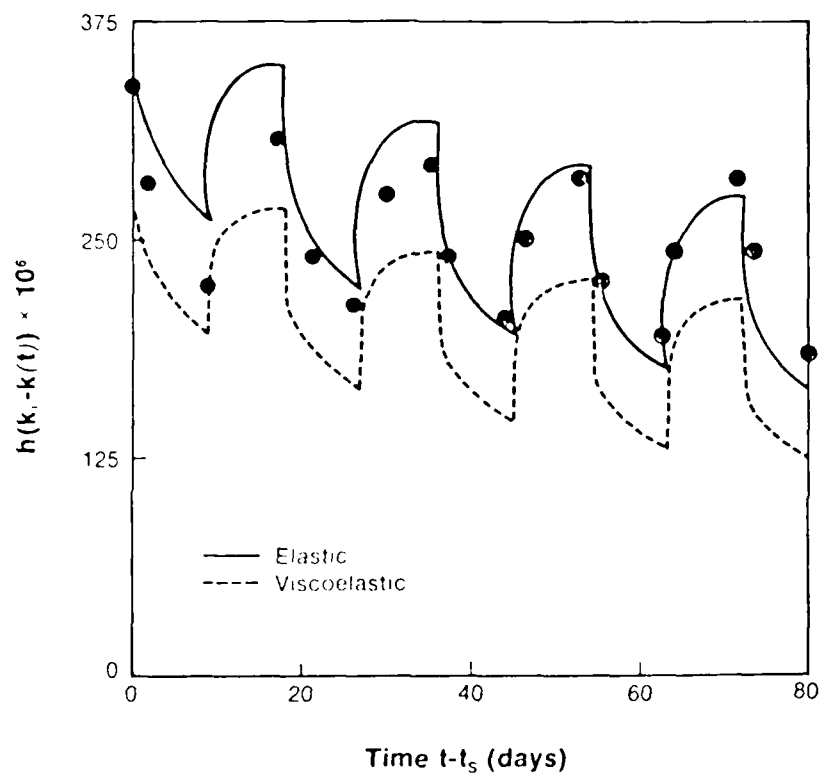


Figure 11. Time-dependent curvature change of  $(0/90/0_4/90_4/0/90)_T$  AS4/3502 graphite/epoxy laminates during cyclic exposure to 0% and 95% relative humidities at 130°F, with cycle interval of 9 days.

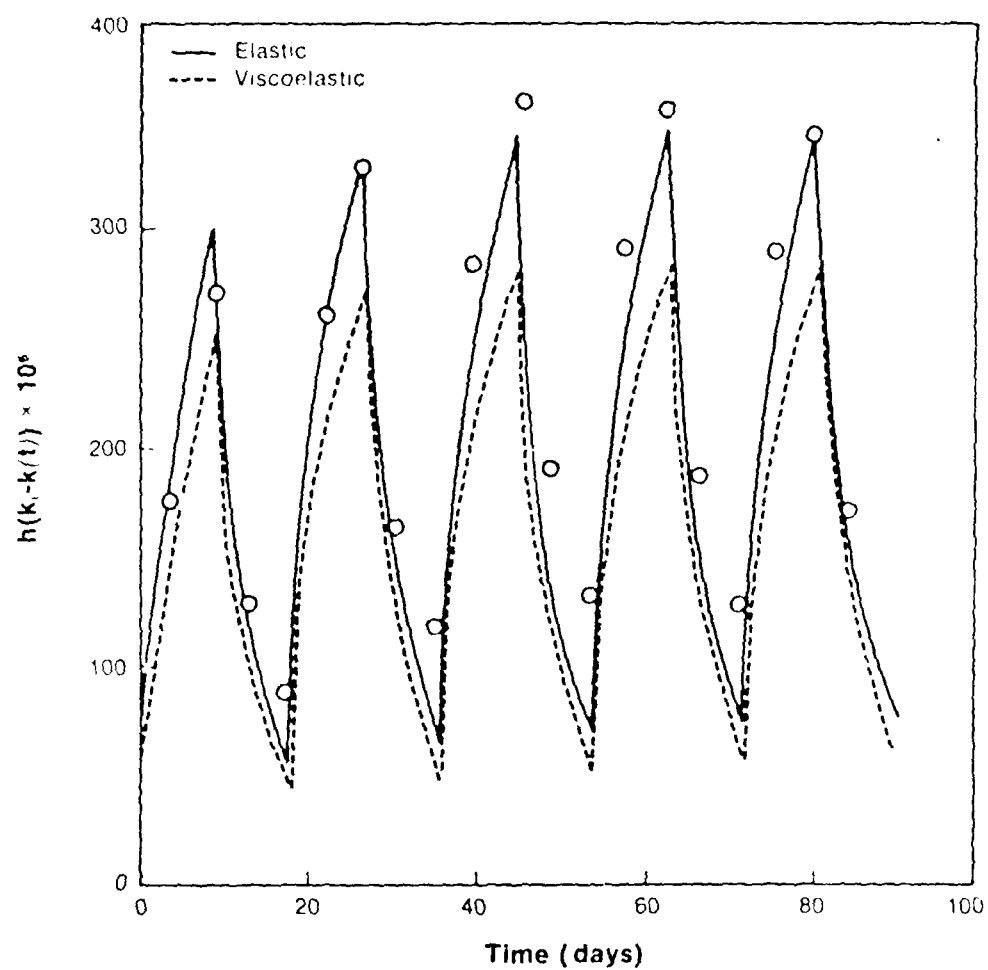


Figure 12. Time-dependent curvature change of  $(0/90/0_4/90_4/0/90)_T$  AS4/3502 graphite/epoxy laminates during cyclic exposure to 0% and 95% relative humidities at 150°F, with cycle interval of 9 days.

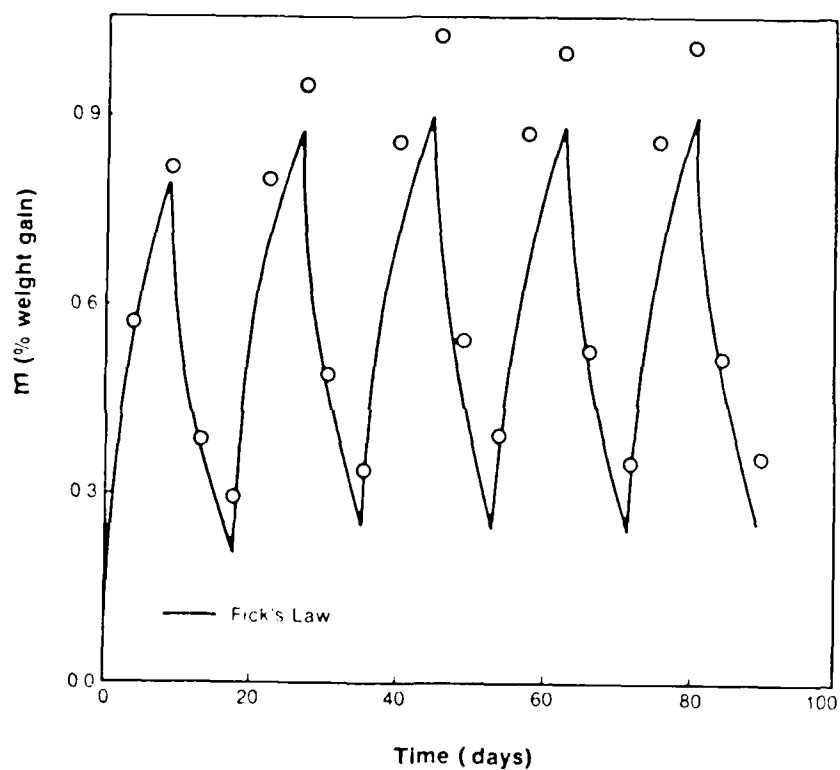


Figure 13. Moisture content (in % weight gain) during cyclic exposure to 0% and 95% relative humidities at 150°F, with cycle interval of 9 days.

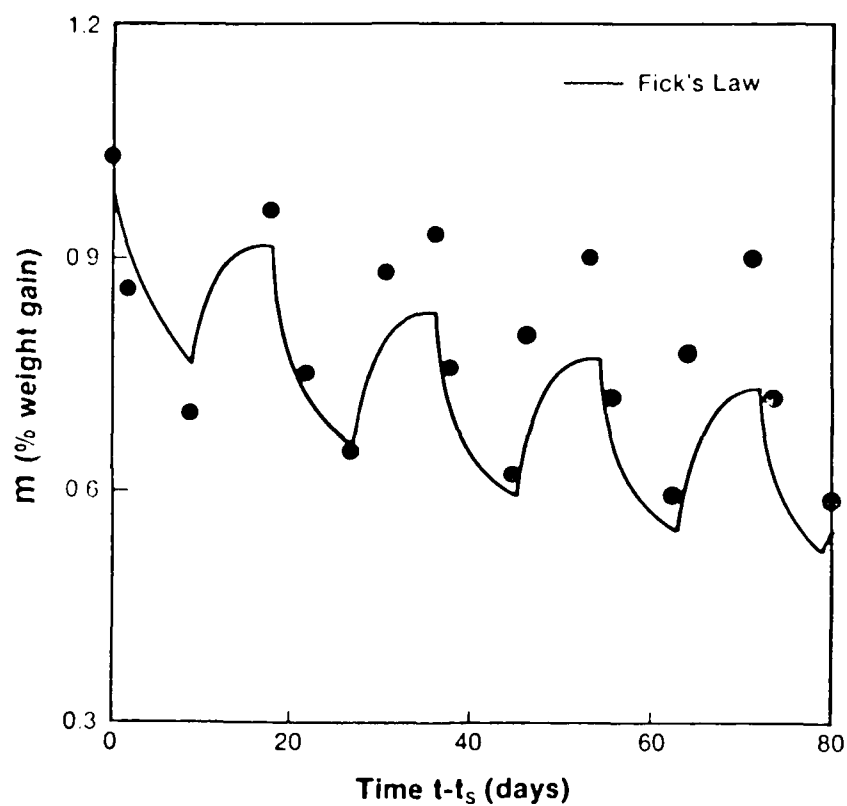


Figure 14. Moisture content (in % weight gain) during cyclic exposure to 0% and 95% relative humidities at 130°F, with cyclic interval of 9 days.

theory ("Fick's law").

Inspection of Figs. 11-14 shows increasing departures between data and theoretical computations. These departures are most likely attributable to the presence and growth of damage, which was not incorporated into the theoretical analyses and predictions of refs. [17] and [36]. The growth and location of damage in the anti-symmetric plates, in relation to the moisture-exposure history, is sketched in Fig. 15 below.

The experimental observations exhibited in Figs. 8-14, as well as in Figs. 4, 5 and 7, support qualitatively the general trends of the damage theory developed in this paper.

## Damage Progression

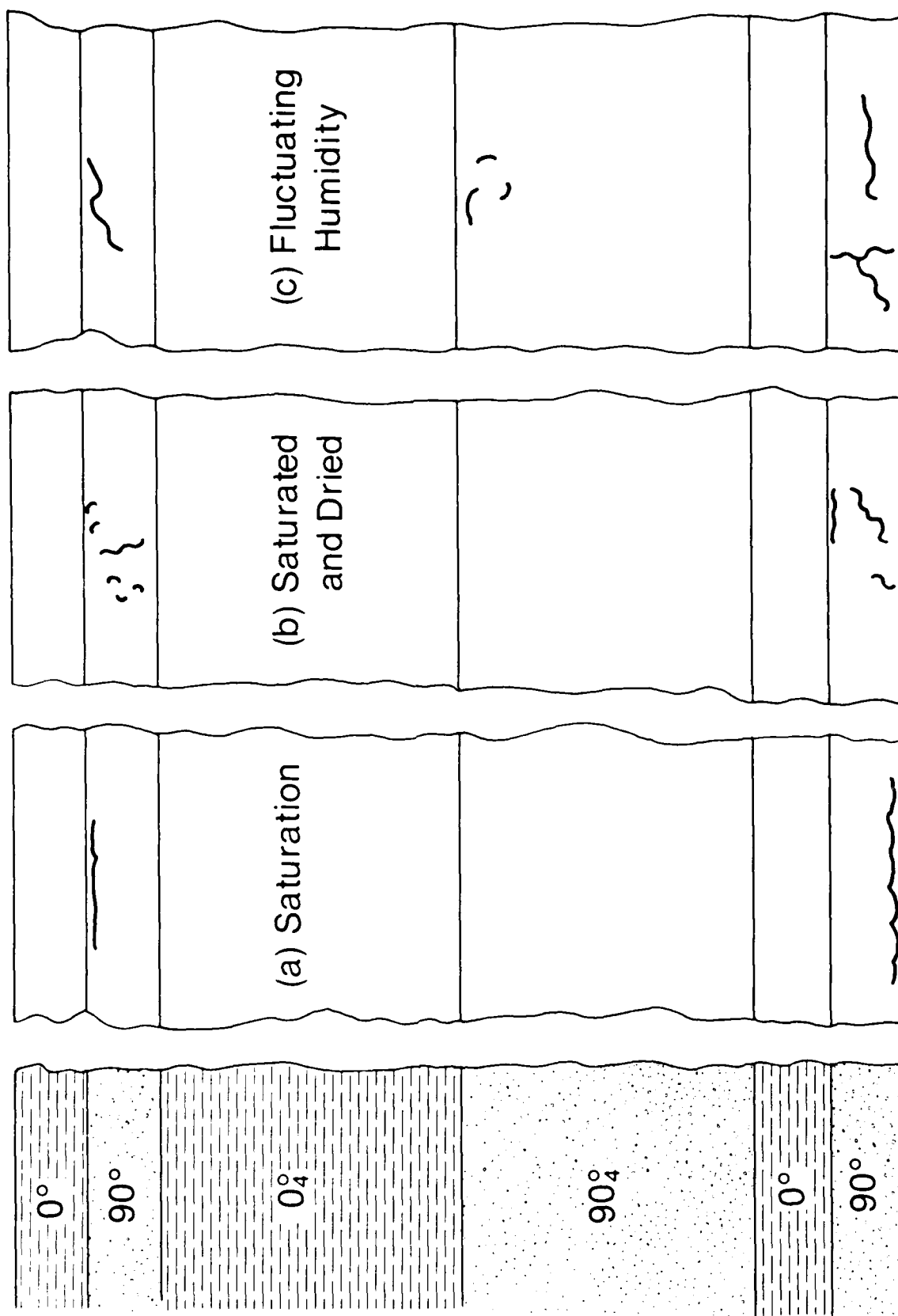


Fig. 15: A sketch of damage progression in a  $[0, 90, 0_4, 90_4, 0, 90]_T$  AS4/3502, Gr/Ep laminate with exposure to moisture. Shown at each stage are damage patterns that developed in addition to previous damage.



### Conclusions

A continuum damage model was developed for a unidirectionally-reinforced, polymeric-resin composite that absorbs moisture from a humid ambient environment. Damage was interpreted as the total cross-sectional area of microcracks that occur within a characteristic material cell prior to the formation of a dominant crack. The total microcracked area was non dimensionalized through division by the respective areas of the cell's walls and was represented by a skew symmetric, second rank, tensor valued, internal state variable.

Moisture ingress into the composite was treated in the context of the thermodynamics of open systems and coupled moisture, stress and damage relations were derived from fundamental principles of thermodynamics and continuum mechanics. These relations included formal expressions for the evolution of damage, for stress-and-damage-coupled diffusion, as well as for damage-dependent material compliances.

It was shown that experimental observations of moisture induced damage, and of moisture absorption and desorption in the presence and absence of stress, tended to verify some of the salient aspects featured in the continuum damage model proposed in this work.

The present work did not provide explicit expressions for the evolution of damage or any of the other formal relations. This deficiency is due to the paucity in data that are available at the present time.

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APPENDIX: TRANSVERSE ISOTROPY, T-4 SYMMETRY (about  $X_3$  axis)

Case of one symmetric tensor  $A_{ij}$ ,  
 one anti-symmetric tensor  $W_{ij}$ ,  
 and one vector  $V_i$

## 1. INVARIANTS:

$$I_1 = A_{33}, I_2 = A_{11} + A_{22}, I_3 = (A_{11} - A_{22})^2 + 4A_{12}^2, I_4 = A_{31}^2 + A_{32}^2,$$

$$I_5 = W_{31}^2 + W_{32}^2, I_6 = A_{31} W_{31} + A_{32} W_{32}, I_7 = V_1^2 + V_2^2, I_8 = V_3^2,$$

$$I_9 = W_{12}^2,$$

$$\begin{bmatrix} I_{10} \\ I_{11} \\ I_{12} \end{bmatrix} = (A_{11} - A_{22}) \begin{bmatrix} A_{31}^2 - A_{32}^2 \\ A_{31} W_{31} - A_{32} W_{32} \\ W_{31}^2 - W_{32}^2 \end{bmatrix} + 2A_{12} \begin{bmatrix} 2A_{31} A_{32} \\ A_{31} W_{32} + A_{32} W_{31} \\ 2W_{31} W_{32} \end{bmatrix}$$

$$I_{13} = (A_{11} - A_{22}) (V_1^2 - V_2^2) + 4A_{12} V_1 V_2,$$

$$\begin{bmatrix} I_{14} \\ I_{15} \\ I_{16} \end{bmatrix} = (V_1^2 - V_2^2) \begin{bmatrix} A_{31}^2 - A_{32}^2 \\ A_{31} W_{31} - A_{32} W_{32} \\ W_{31}^2 - W_{32}^2 \end{bmatrix} + 2V_1 V_2 \begin{bmatrix} 2A_{31} A_{32} \\ A_{31} W_{32} + A_{32} W_{31} \\ 2W_{31} W_{32} \end{bmatrix}$$

$$\begin{bmatrix} I_{17} \\ I_{18} \end{bmatrix} = V_3 \begin{bmatrix} A_{31} V_1 + A_{32} V_2 \\ W_{31} V_1 + W_{32} V_2 \end{bmatrix}, \quad I_{19} = W_{12} (A_{31} W_{32} - A_{32} W_{31}),$$

$$I_{20} = [(A_{11} - A_{22}) V_1 V_2 - A_{12} (V_1^2 - V_2^2)] (A_{31} W_{32} - A_{32} W_{31}),$$

$$\begin{bmatrix} I_{21} \\ I_{22} \\ I_{23} \end{bmatrix} = W_{12} \left\{ (A_{11} - A_{22}) \begin{bmatrix} 2A_{31} A_{32} \\ A_{31} W_{32} + A_{32} W_{31} \\ 2W_{31} W_{32} \end{bmatrix} - 2A_{12} \begin{bmatrix} A_{31}^2 - A_{32}^2 \\ A_{31} W_{31} - A_{32} W_{32} \\ W_{31}^2 - W_{32}^2 \end{bmatrix} \right\}$$

$$I_{24} = W_{12} [(A_{11} - A_{22}) V_1 V_2 - A_{12} (V_1^2 - V_2^2)]$$

$$\begin{bmatrix} I_{25} \\ I_{26} \\ I_{27} \end{bmatrix} = W_{12} \left\{ 2 \begin{bmatrix} A_{31}^2 - A_{32}^2 \\ A_{31} W_{31} - A_{32} W_{32} \\ W_{31}^2 - W_{32}^2 \end{bmatrix} V_1 V_2 - \begin{bmatrix} 2A_{31} A_{32} \\ A_{31} W_{32} + A_{32} W_{31} \\ 2W_{31} W_{32} \end{bmatrix} (V_1^2 - V_2^2) \right\}$$

$$\begin{bmatrix} I_{28} \\ I_{29} \end{bmatrix} = V_3 \left\{ (A_{11} - A_{22}) \begin{bmatrix} A_{31} V_1 - A_{32} V_2 \\ W_{31} V_1 - W_{32} V_2 \end{bmatrix} + 2A_{12} \begin{bmatrix} A_{31} V_2 + A_{32} V_1 \\ W_{31} V_2 + W_{32} V_1 \end{bmatrix} \right\}$$

$$\begin{bmatrix} I_{30} \\ I_{31} \end{bmatrix} = V_3 W_{12} \begin{bmatrix} A_{31} V_2 - A_{32} V_1 \\ W_{31} V_2 - W_{32} V_1 \end{bmatrix}$$

$$\begin{bmatrix} I_{32} \\ I_{33} \end{bmatrix} = V_3 W_{12} \left\{ (A_{11} - A_{22}) \begin{bmatrix} A_{31} V_2 + A_{32} V_1 \\ W_{31} V_2 + W_{32} V_1 \end{bmatrix} - 2A_{12} \begin{bmatrix} A_{31} V_1 - A_{32} V_2 \\ W_{31} V_1 - W_{32} V_2 \end{bmatrix} \right\}$$



## 2. VECTOR-VALUED FUNCTIONS

$$u_1 = P_1 V_1 + P_2 [(A_{11} - A_{22}) V_1 + 2A_{12} V_2] + P_3 (A_{31} W_{32} - A_{32} W_{31}) V_2$$

$$+ \begin{bmatrix} P_4 \\ P_5 \\ P_6 \end{bmatrix} \left\{ \begin{bmatrix} A_{31}^2 - A_{32}^2 \\ A_{31} W_{31} - A_{32} W_{32} \\ W_{31}^2 - W_{32}^2 \end{bmatrix} V_1 + \begin{bmatrix} 2A_{31} A_{32} \\ A_{31} W_{32} + A_{32} W_{31} \\ 2W_{31} W_{32} \end{bmatrix} V_2 \right\}$$

$$+ \begin{bmatrix} P_7 \\ P_8 \end{bmatrix} V_3 \begin{bmatrix} A_{31} \\ W_{31} \end{bmatrix} + P_9 W_{12} V_2$$

$$+ \begin{bmatrix} P_{10} \\ P_{11} \\ P_{12} \end{bmatrix} \left\{ (A_{11} - A_{22}) \begin{bmatrix} 2A_{31} A_{32} \\ A_{31} W_{32} + A_{32} W_{31} \\ 2W_{31} W_{32} \end{bmatrix} - 2A_{12} \begin{bmatrix} A_{31}^2 - A_{32}^2 \\ A_{31} W_{31} - A_{32} W_{32} \\ W_{31}^2 - W_{32}^2 \end{bmatrix} \right\} V_2$$

$$+ P_{13} [(A_{11} - A_{22}) V_2 - 2A_{12} V_1] (A_{31} W_{32} - A_{32} W_{31})$$

$$+ P_{14} [(A_{11} - A_{22}) V_2 - 2A_{12} V_1] W_{12}$$

$$+ \begin{bmatrix} P_{15} \\ P_{16} \\ P_{17} \end{bmatrix} W_{12} \left\{ \begin{bmatrix} A_{31}^2 - A_{32}^2 \\ A_{31} W_{31} - A_{32} W_{32} \\ W_{31}^2 - W_{32}^2 \end{bmatrix} V_2 - \begin{bmatrix} 2A_{31} A_{32} \\ A_{31} W_{32} + A_{32} W_{31} \\ 2W_{31} W_{32} \end{bmatrix} V_1 \right\}$$

$$\begin{aligned}
& + \begin{bmatrix} P_{18} \\ P_{19} \end{bmatrix} V_3 \left\{ (A_{11} - A_{22}) \begin{bmatrix} A_{31} \\ W_{31} \end{bmatrix} + 2A_{12} \begin{bmatrix} A_{32} \\ W_{32} \end{bmatrix} \right\} + \begin{bmatrix} P_{20} \\ P_{21} \end{bmatrix} V_3 W_{12} \begin{bmatrix} A_{32} \\ W_{32} \end{bmatrix} \\
& + \begin{bmatrix} P_{22} \\ P_{23} \end{bmatrix} V_3 W_{12} \left\{ (A_{11} - A_{22}) \begin{bmatrix} A_{32} \\ W_{32} \end{bmatrix} - 2A_{12} \begin{bmatrix} A_{31} \\ W_{31} \end{bmatrix} \right\}
\end{aligned}$$

$$u_2 = P_1 V_2 + P_2 [-(A_{11} - A_{22}) V_2 + 2A_{12} V_1] - P_3 (A_{31} W_{32} - A_{32} W_{31}) V_1$$

$$+ \begin{bmatrix} P_4 \\ P_5 \\ P_6 \end{bmatrix} \left\{ - \begin{bmatrix} A_{31}^2 - A_{32}^2 \\ A_{31} W_{31} - A_{32} W_{32} \\ W_{31}^2 - W_{32}^2 \end{bmatrix} V_2 + \begin{bmatrix} 2A_{31} A_{32} \\ A_{31} W_{32} + A_{32} W_{31} \\ 2W_{31} W_{32} \end{bmatrix} V_1 \right\}$$

$$+ \begin{bmatrix} P_7 \\ P_8 \end{bmatrix} V_3 \begin{bmatrix} A_{32} \\ W_{32} \end{bmatrix} - F_9 W_{12} V_1$$

$$- \begin{bmatrix} P_{10} \\ P_{11} \\ P_{12} \end{bmatrix} \left\{ (A_{11} - A_{22}) \begin{bmatrix} 2A_{31} A_{32} \\ A_{31} W_{32} + A_{32} W_{31} \\ 2W_{31} W_{32} \end{bmatrix} - 2A_{12} \begin{bmatrix} A_{31}^2 - A_{32}^2 \\ A_{31} W_{31} - A_{32} W_{32} \\ W_{31}^2 - W_{32}^2 \end{bmatrix} \right\} V_1$$

$$+ P_{13} [(A_{11} - A_{22}) V_1 + 2A_{12} V_2] (A_{31} W_{32} - A_{32} W_{31})$$

$$+ P_{14} [(A_{11} - A_{22}) V_1 + 2A_{12} V_2] W_{12}$$

$$\begin{aligned}
& + \begin{bmatrix} P_{15} \\ P_{16} \\ P_{17} \end{bmatrix} W_{12} \left\{ \begin{bmatrix} A_{31}^2 - A_{32}^2 \\ A_{31} W_{31} - A_{32} W_{32} \\ W_{31}^2 - W_{32}^2 \end{bmatrix} V_1 + \begin{bmatrix} 2A_{31} A_{32} \\ A_{31} W_{32} + A_{32} W_{31} \\ 2W_{31} W_{32} \end{bmatrix} V_2 \right\} \\
& + \begin{bmatrix} P_{18} \\ P_{19} \end{bmatrix} V_3 \left\{ - (A_{11} - A_{22}) \begin{bmatrix} A_{32} \\ W_{32} \end{bmatrix} + 2A_{12} \begin{bmatrix} A_{31} \\ W_{31} \end{bmatrix} \right\} - \begin{bmatrix} F_{20} \\ F_{21} \end{bmatrix} V_3 W_{12} \begin{bmatrix} A_{31} \\ W_{31} \end{bmatrix} \\
& + \begin{bmatrix} P_{22} \\ P_{23} \end{bmatrix} V_3 W_{12} \left\{ (A_{11} - A_{22}) \begin{bmatrix} A_{31} \\ W_{31} \end{bmatrix} + 2A_{12} \begin{bmatrix} A_{32} \\ W_{32} \end{bmatrix} \right\}
\end{aligned}$$

$$u_3 = H_1 V_3$$

$$+ \begin{bmatrix} H_2 \\ H_3 \end{bmatrix} \begin{bmatrix} A_{31} V_1 + A_{32} V_2 \\ W_{31} V_1 + W_{32} V_2 \end{bmatrix}$$

$$+ \begin{bmatrix} H_4 \\ H_5 \end{bmatrix} \left\{ (A_{11} - A_{22}) \begin{bmatrix} A_{31} V_1 - A_{32} V_2 \\ W_{31} V_1 - W_{32} V_2 \end{bmatrix} + 2A_{12} \begin{bmatrix} A_{31} V_2 + A_{32} V_1 \\ W_{31} V_2 + W_{32} V_1 \end{bmatrix} \right\}$$

$$+ \begin{bmatrix} H_6 \\ H_7 \end{bmatrix} W_{12} \left\{ \begin{bmatrix} A_{31} V_2 - A_{32} V_1 \\ W_{31} V_2 - W_{32} V_1 \end{bmatrix} \right\}$$

$$+ \begin{bmatrix} H_8 \\ H_9 \end{bmatrix} W_{12} \left\{ (A_{11} - A_{22}) \begin{bmatrix} A_{31} V_2 + A_{32} V_1 \\ W_{31} V_2 + W_{32} V_1 \end{bmatrix} - 2A_{12} \begin{bmatrix} A_{31} V_1 - A_{32} V_2 \\ W_{31} V_1 - W_{32} V_2 \end{bmatrix} \right\}$$

3. SKEW-SYMMETRIC TENSOR VALUED FUNCTIONS

$$\begin{aligned}
W_{31} = & r_1 W_{31} + r_2 [(A_{11} - A_{22})W_{31} + A_{12}W_{32} - A_{32}W_{12}] + r_3 V_2 (V_1 A_{32} - V_3 A_{12}) \\
& + r_4 [(V_1^2 - V_2^2)W_{31} + V_2 (V_1 W_{32} - V_3 W_{12})] + r_5 (W_{12} A_{32} - W_{32} A_{12}) \\
& + r_6 (A_{11} - A_{12})V_2 (V_1 A_{32} - V_3 A_{12}) \\
& + r_7 [(A_{11} - A_{22})V_2 (V_1 W_{32} - V_3 W_{12}) - 2(V_1^2 - V_2^2)(A_{12}W_{32} - A_{32}W_{12})] \\
& + r_8 [(A_{11} - A_{22})(W_{12}A_{32} - W_{32}A_{12})] + r_9 W_{12} A_{12} W_{31} \\
& + r_{10} [(W_{12} A_{32} - W_{32} A_{12})(V_1^2 - V_2^2)] + r_{11} W_{12} W_{31} V_1 V_2 \\
& + r_{12} V_2 (A_{12} V_3 - A_{32} V_1) + r_{13} V_2 (W_{12} V_3 - W_{32} V_1) \\
& + r_{14} (A_{11} - A_{22})V_2 (W_{12} V_3 - W_{32} V_1)
\end{aligned}$$

$$\begin{aligned}
W_{32} = & r_1 W_{32} + r_2 [-(A_{11} - A_{22})W_{32} + A_{12}W_{31} - A_{13}W_{21}] + r_3 V_1 (V_2 A_{31} - V_3 A_{21}) \\
& + r_4 [-(V_1^2 - V_2^2)W_{32} + V_1 (V_2 W_{31} - V_3 W_{21})] - r_5 (W_{12} A_{31} - W_{13} A_{21}) \\
& - r_6 (A_{11} - A_{22})V_1 (V_2 A_{31} - V_3 A_{21}) \\
& - r_7 [(A_{11} - A_{22})V_1 (V_2 W_{31} - V_3 W_{21}) - 2(V_1^2 - V_2^2)(A_{12}W_{31} - A_{13}W_{21})] \\
& + r_8 [(A_{11} - A_{22})(W_{12} A_{31} - W_{13} A_{21})] - r_9 W_{12} A_{12} W_{32} \\
& + r_{10} [(W_{12} A_{31} - W_{13} A_{21})(V_1^2 - V_2^2)] - r_{11} W_{12} W_{32} V_1 V_2 \\
& + r_{12} V_1 (A_{12} V_3 - A_{13} V_2) - r_{13} V_1 (V_3 W_{12} - V_2 W_{13}) \\
& + r_{14} (A_{11} - A_{22})V_1 (W_{12} V_3 - W_{13} V_2)
\end{aligned}$$

$$\begin{aligned}
W_{12} = & h_1 W_{12} + h_2 (A_{31} W_{32} - A_{32} W_{31}) + h_3 V_3 (A_{31} V_2 - A_{32} V_1) \\
& + h_4 V_3 (W_{31} V_2 - W_{32} V_1)
\end{aligned}$$

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